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Baseline groundwater chemistry: the Palaeogene of the Thames Basin

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Baseline groundwater chemistry: the Palaeogene of the Thames Basin

J M Bearcock and P L Smedley

Keywords

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Map

Sheet 999, 1:99 000 scale, Map name

Front cover

Palaeogene exposure at Upnor [TQ 765 705]. Ferruginous Woolwich Formation sands are overlain by pebbly and shelly Harwich Formation, and a thin layer of blueish London Clay, beneath the drift at the top of the section. (Photograph: J. M. Pulsford)

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Foreword

Although groundwater has long been seen as a relatively pure natural resource stored in subsurface aquifers, its quality is under an ever-increasing threat from human influences. Changes in chemical quality occur through direct inputs of anthropogenic substances, through groundwater abstraction and resultant change in groundwater flow regimes and through artificial recharge. Groundwater is an important resource for drinking, agricultural, industrial and domestic supply. About 35 per cent of public water supply in England and Wales and more than 70% in south and east England is provided by groundwater resources. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater. Monitoring, management and protection of groundwater quantity and quality are therefore important economic and environmental priorities.

Characterisation and monitoring of groundwater chemistry is a critical component of management and protection. This provides the basis for defining the suitability of groundwater for its intended purpose, identifying pollution inputs and assessing any temporal change. The main European driver for the characterisation and monitoring of groundwater quality is European Union legislation in the form of the Water Framework Directive, Groundwater Directive, EC drinking-water regulations and environmental-quality standards. A key starting point for aquifer protection is defining the natural or 'baseline' chemistry of the groundwater body concerned. This sets the framework against which anthropogenic impacts and trends can be measured.

The concept of 'baseline' in the context of groundwater quality is difficult to define in detail and opinions differ on the meaning and application of the term. The presence of purely anthropogenic substances such as pesticides or CFCs indicates a departure from the natural condition, but for many solutes which can be derived either from pollution or natural sources, for example nitrate, phosphorus or arsenic, the distinction is less clear-cut. In addition, specific chemical constituents in a given groundwater body may be identified as pollutants while other component solutes may be entirely naturally-derived. For the purposes of this study, baseline is defined as:

> "*the range in concentration (within a specified system) of an element, species or chemical substance present in solution which is derived by natural processes from natural geological, biological, or atmospheric sources*".

The baseline chemistry of groundwater varies widely as a function of the many complex geological, geochemical, hydrogeological and climatic factors. These give rise to large spatial and temporal variations in chemical quality, at a range of scales. Hence, the baseline for a given element or compound will vary significantly both between and within aquifers. It is, therefore, scale-dependent and should be considered as a range rather than a single value.

Attempting to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England and Wales has been the objective of the project 'Baseline'. The project involves the characterisation of spatial and temporal variations in groundwater chemistry and interpretation of the dominant controlling processes within a given area, aquifer or aquifer block. For each study area, this has been achieved through collation of existing reliable groundwater, rainfall, land-use and host-aquifer mineralogical and geochemical data, as well as new strategic sampling of typically 25–30 groundwater sources for a comprehensive suite of inorganic constituents. Selected analysis of stable-isotopic compositions (e.g. O, H, C) and atmospheric tracers (CFCs, SF_6) has also been undertaken where appropriate. Statistical methods, including statistical summaries (medians, arithmetic means, percentiles), together with box plots and cumulative-probability diagrams, provide some of the most valuable analytical tools for the assessment of chemical data and

have been used in the Baseline report series. The Baseline reports provide a summary of the inorganic chemical status of groundwaters in a given study area and key pressures on water quality which should provide useful background information of value to water regulators and managers, environmental scientists and water users.

The current series of Baseline reports has been produced by the British Geological Survey with funding from the Natural Environment Research Council. This follows on from a previous series which was produced in collaboration with, and with co-funding from, the Environment Agency.

Previous published reports in the Baseline Series (British Geological Survey – Environment Agency):

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4. The Chalk of Dorset
5. The Chalk of the North Downs
6. The Chalk of the Colne and Lee River Catchments
7. The Great and Inferior Oolite of the Cotswolds District
8. The Permo-Triassic Sandstones of Manchester and East Cheshire
9. The Lower Greensand of southern England
10. The Chalk of Yorkshire and North Humberside
11. The Bridport Sands of Dorset and Somerset
12. The Devonian aquifer of South Wales and Herefordshire
13. The Great Ouse Chalk aquifer
14. The Corallian of Oxfordshire and Wiltshire
15. The Palaeogene of the Wessex Basin
16. The Granites of South-West England
17. The Ordovician and Silurian meta-sedimentary aquifers of central and south-west Wales
18. The Millstone Grit of Northern England
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20. The Permo-Triassic Sandstone aquifer of Shropshire
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The Chalk aquifer of Hampshire
The Magnesian Limestone of County Durham and north Yorkshire

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Summary

This report describes the regional geochemistry of groundwater from the Palaeogene aquifer of the Thames Basin. The aim of the study is to assess the likely natural baseline chemistry of the groundwater by identifying the dominant controlling processes. Data have been collected from strategic sampling of 19 new groundwater samples, along with collation, from various sources, of existing groundwater, rainfall, mineralogical and geochemical data.

The Palaeogene aquifer results from the cyclical deposition of shallow marine and coastal sediments and comprises sand and clay layers which display large lateral and vertical variation. This variation gives rise to localised regions of productive aquifer, and localised geochemical variations. For these reasons the Palaeogene strata only provide minor aquifers of regional significance. That said, these can be important when managing the water supply in London and the surrounding urbanised areas.

The geological differences between formations within the Palaeogene strata mean that the water type is generally a continuum between Ca-HCO_3 type to Ca-SO_4 type. Other differences in groundwater quality caused by geological variation are evident in the minor and trace element concentrations.

The main water quality problems are associated with oxidation of pyrite, which occurs sporadically throughout the Palaeogene beds, and has the ability to produce acidic, hard, metal-rich waters. In beds underlying the confining London Clay, this has occurred as a result of anthropogenic groundwater extraction from the Chalk below. In beds above the London Clay this process can occur entirely naturally, owing to a ready supply of oxygen and water.

In addition human impacts are mainly visible in the presence of indicator contaminants, such as nitrate. The widespread presence and increasing concentrations of nitrate indicate the extent to which the unconfined aquifer is influenced by modern farming practices or urban pollution. Trace metals associated with the oxidation of pyrite within the aquifer (Fe, Ni, Co) also affect the water quality. Whilst these are released as a result of natural geochemical reactions, historic pumping regimes have also exerted an influence. Lead is found in elevated concentrations (up to 13.3 $\mu g\ L^{-1}$) in samples taken in close proximity to major roads, and it is likely that these derive from the past usage of leaded petrol in motor vehicles.

While some of the groundwaters investigated in this study are of good inorganic quality, and of a soft nature, there are many notable exceptions which contain elevated concentrations of Fe, SO_4, Ni and Co. The distribution of these is generally so sporadic that water quality would be difficult to predict prior to drilling a borehole. It is recommended to drill into the underlying Chalk for a groundwater source of more reliable quality and quantity.

1 Introduction

This study concerns the portion of the Palaeogene strata which forms the Thames Basin. The outcrop occupies a wedge-shaped outcrop, which extends from Durley [SU 23 64] near Marlborough [SU 19 69] in the west, to Orford Ness [TM 46 50] in the north-east and Ramsgate [TR 35 64] in the south-west. The aquifer is composed of sands and clays, and while it is not a regionally important aquifer, the Palaeogene of the Thames Basin can be important locally, for managing the water supply in the most densely populated area of the UK.

This report characterises the groundwater chemistry in the Thames Basin, outlining spatial, and temporal variability and assessing the likely controls and ranges of baseline concentrations.

2 Geographical setting

2.1 STUDY LOCATION

The Thames Basin Palaeogene outcrop is a wedge which covers the lower parts of the Thames Valley and the fringes of the Thames Estuary. The sample sites in this study were taken from sites in Berkshire, Essex and Kent, extending over an area of approximately 7,000 km^2. Figure 2.1 shows the extent of the Palaeogene strata.

While the Palaeogene aquifers of the Thames Basin are minor in the UK context (Jones et al., 2000), they are important for managing the water supply in the most densely populated areas of the UK. The underlying Chalk forms the major aquifer in the region; it is a reliable, clean water source. For this reason abstractions in the Palaeogene strata are uncommon and vary in number according to local conditions.

2.2 LAND USE AND PHYSICAL FEATURES

Land use variations often relate to differences in topography, climate, soil fertility, and geology (Kelly and Panno, 2008), which in turn can have important implications for groundwater quality. The topography and land use in the area generally reflects the underlying geology. The Palaeogene strata presented in Figure 2.1 are underlain by Cretaceous Chalk. The Cretaceous and Palaeogene strata yield relatively low-lying and flat land. The predominant land uses are arable, grassland, and urban, and there is little coverage of woodland, shrubs, or bogs, which are more commonly associated with upland areas (see

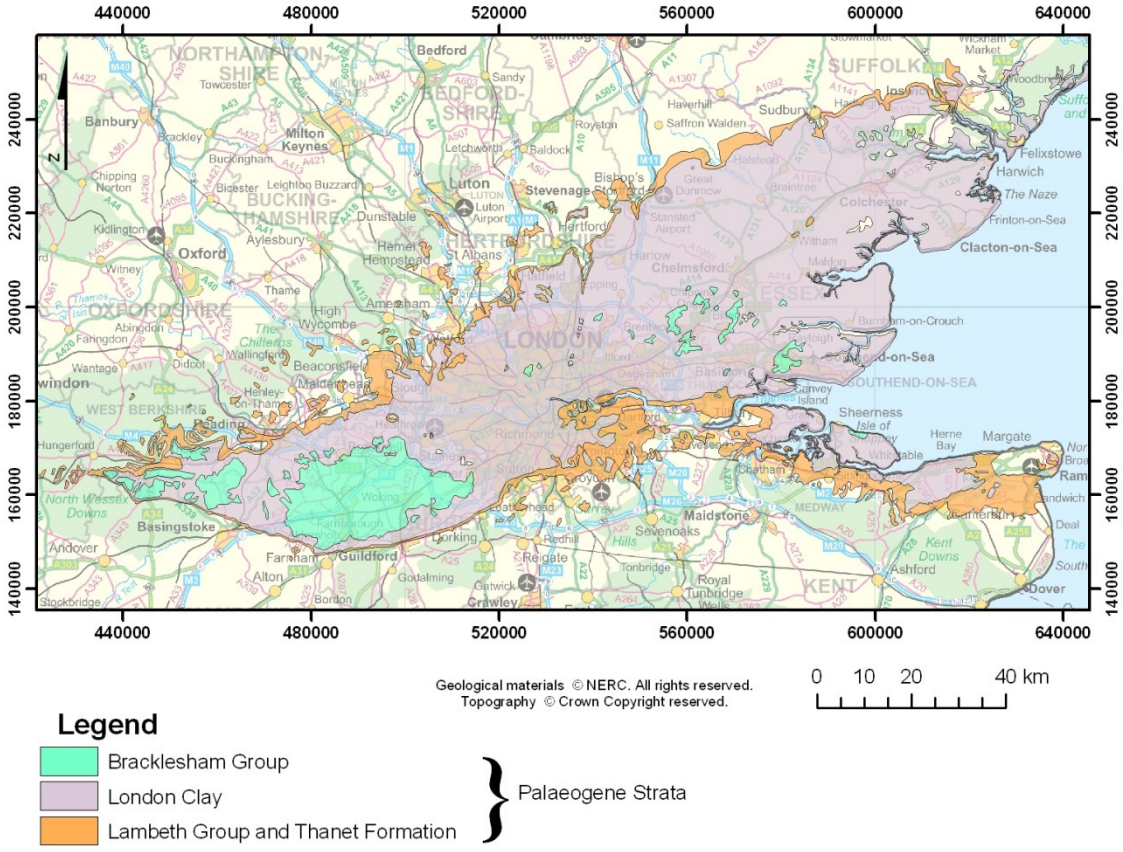

Figure 2.1 Location of Palaeogene strata in the London Basin

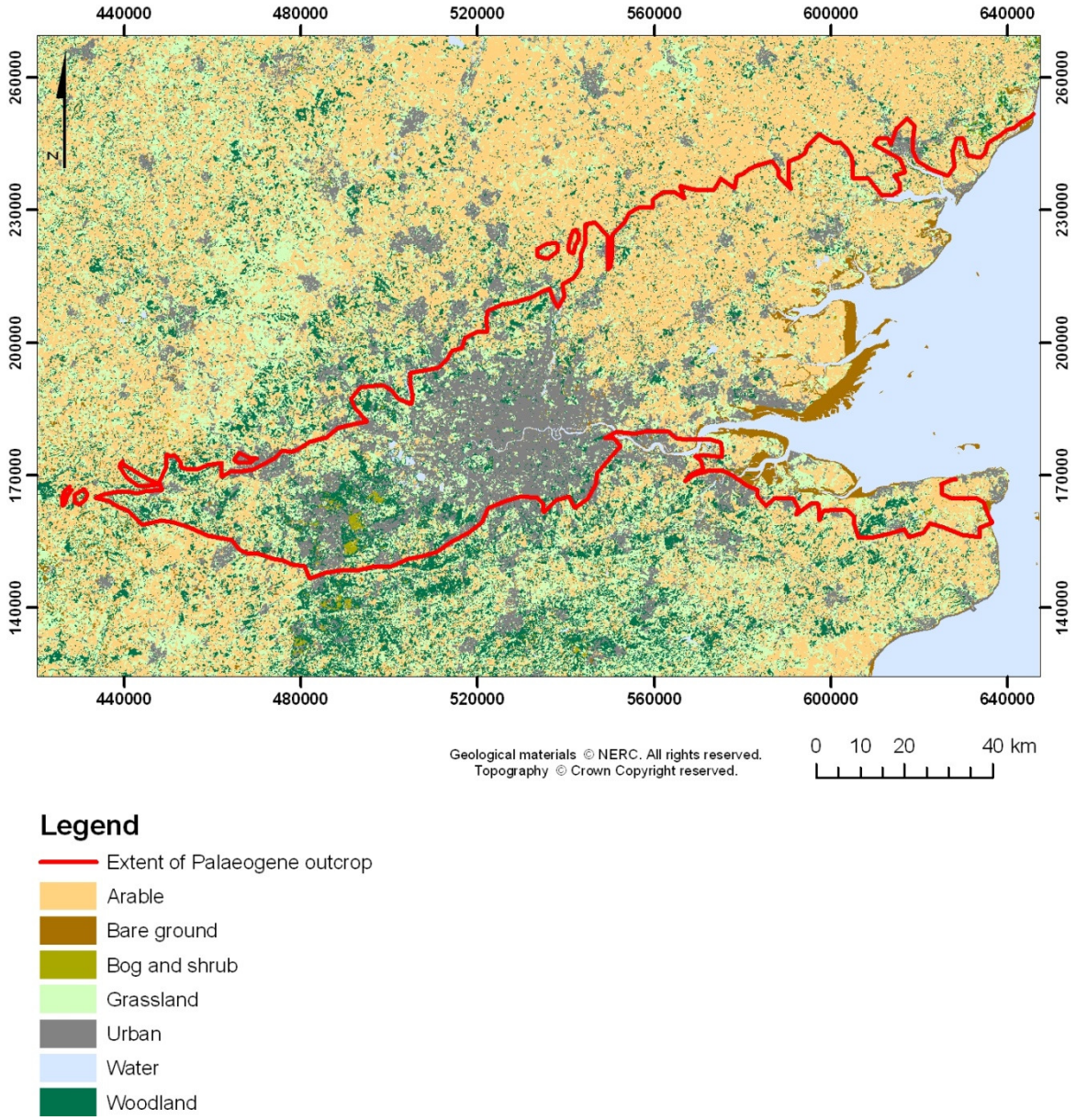

Figure 2.2 Land use in the region around the Paleogene of the London Basin, based on digital spatial data licensed from the Centre for Ecology & Hydrology, © NERC (CEH) (Fuller et al., 2002)

Figure 2.2).The grassland is most commonly found around the periphery of the urban areas. The arable farming can be subdivided into two main types: cereals (e.g. barley, maize, oats, wheat) and horticulture (e.g. carrots, beans, potatoes, rape, beet, mustard). There is roughly equal land cover of cereals and horticulture to the west of the Greater London area. Horticulture predominates to the north-east of Greater London (within approx 35 km), and cereals predominate closer to the coast (up to around 25 km from the coast). To the west of London the vegetation is more varied, reflecting higher ground and hills. Most of the Palaeogene at outcrop is composed of London Clay, but in the west the younger, sandier, Bagshot Formation outcrops give rise to boggier land supporting shrubs and trees

The outcrop pattern of the Palaeogene strata is closely related to its geological structure. This is dominated by the London Basin synclinorium, which is a broad fold and is open to the east. At outcrop the oldest rocks are found at the edge of the syncline and progressively young

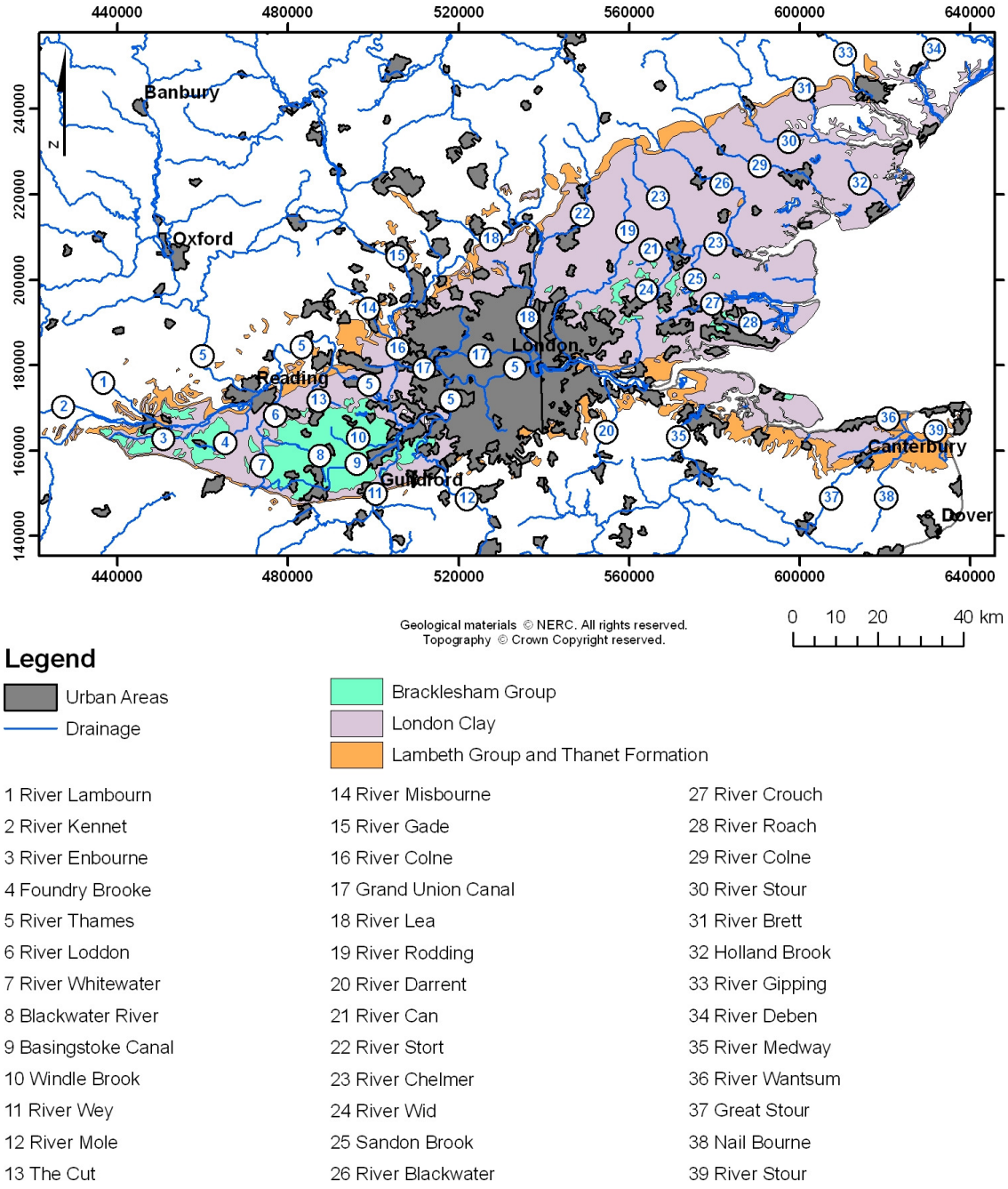

Figure 2.3 Physical features of the Palaeogene of the London Basin

towards the centre. The London Clay is the thickest and most widespread Palaeogene formation (Sumbler, 1996; Ellison et al., 2004).

The main urban areas in the region are built upon the Palaeogene deposits (see Figure 2.2). Besides the Greater London area, there is a band of heavily urbanised land between Reading and Guildford. The predominance of London Clay is partially responsible for the extent of the development of these areas. It can be considered the most important geological formation in the UK from an engineering point of view. This is owing to the quantity and value of structures that are founded on it, and the tunnels that are excavated within it, which include the London Underground system (Sumbler, 1996; Ellison et al., 2004).

The main rivers in the area drain into the centre of the London Basin syncline, and mostly into the River Thames. They tend to be sourced from the Chalk which borders the Palaeogene. Figure 2.3 shows the extensive drainage system influenced by strata of the London Basin Palaeogene. In addition there are substantial areas of stored surface water. There are a group of reservoirs forming the Lee Valley reservoir chain in the north-west of the London urban area (between [TQ 37 97] and [TQ 3488]). Additionally there is a band of reservoirs to the south-west of London extending between Windsor [TQ 96 76] and Walton-on-Thames [TQ 10 66].

The sample sites used in this study are given in Figure 2.4 which also shows the data source (discussed in Section 4.1). Figure 2.5 shows the source aquifers for each of the samples, which generally follow the outcrop pattern. Figure 2.6 shows the location of minor settlements named in this report.

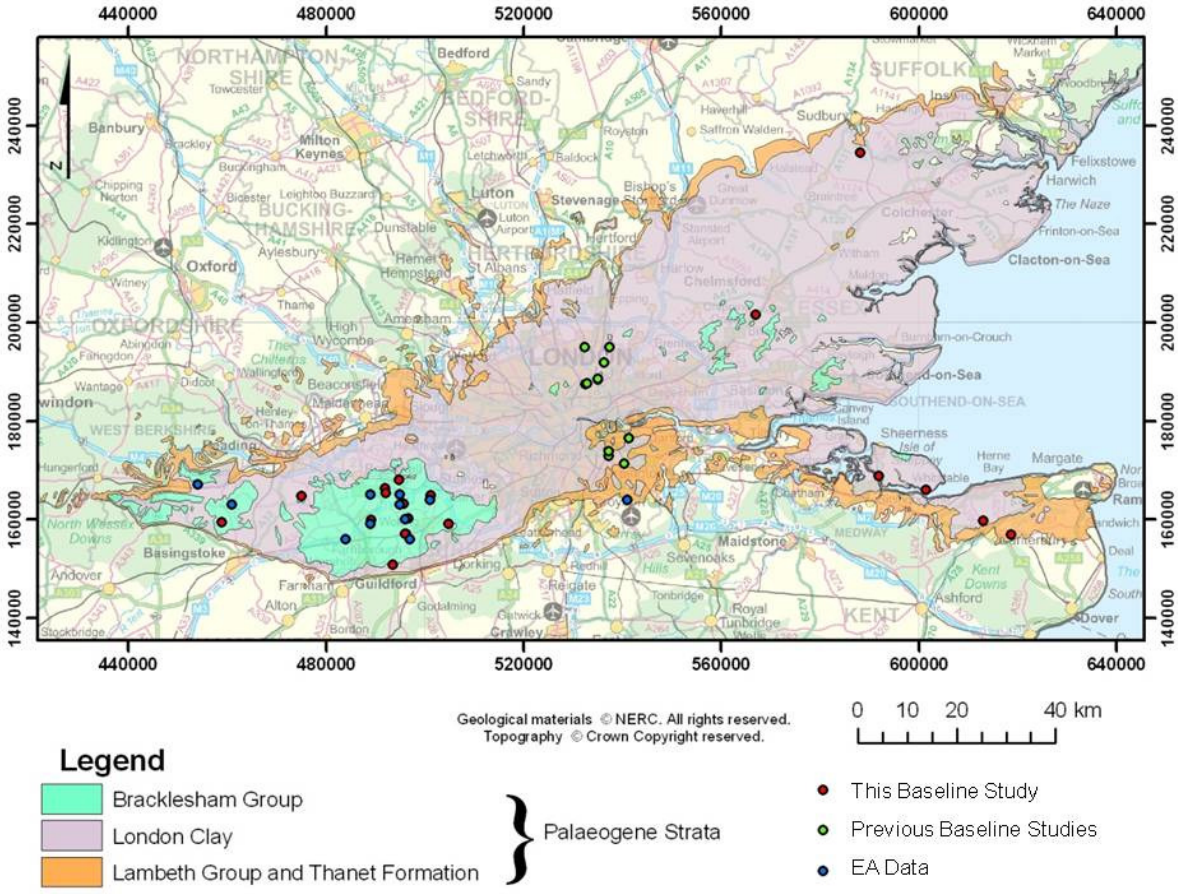

Figure 2.4 Location and data source of sample sites in this study

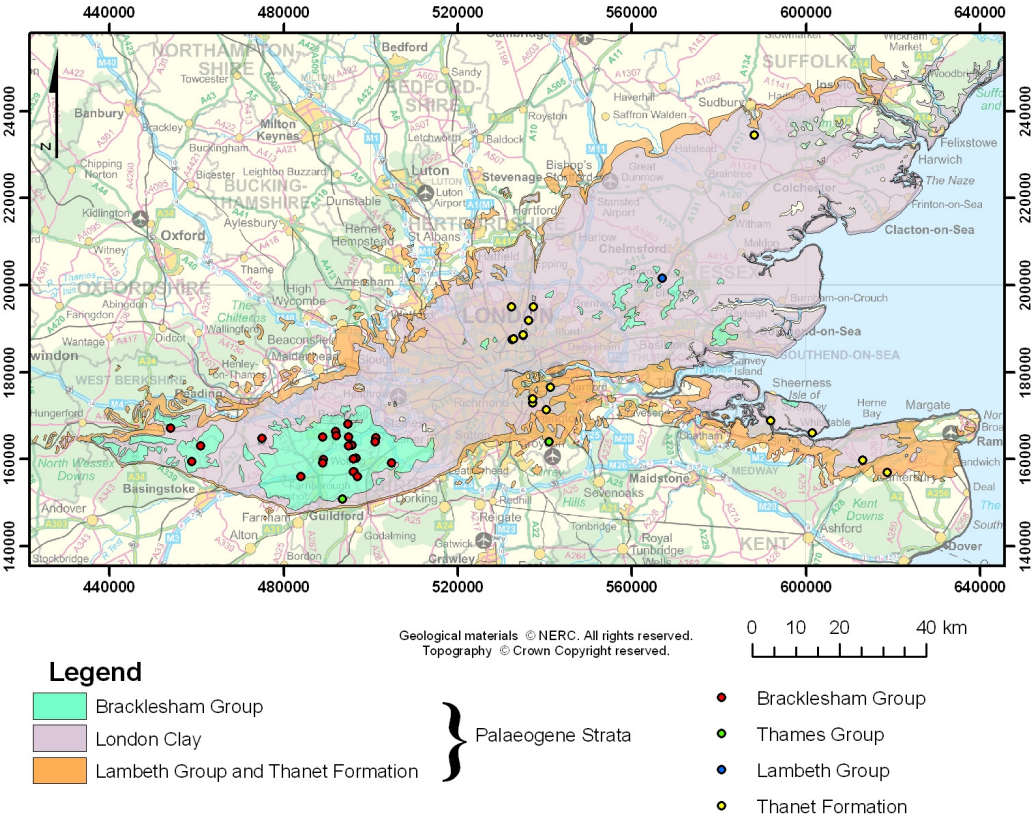

Figure 2.5 Location and sample source of sites in this study

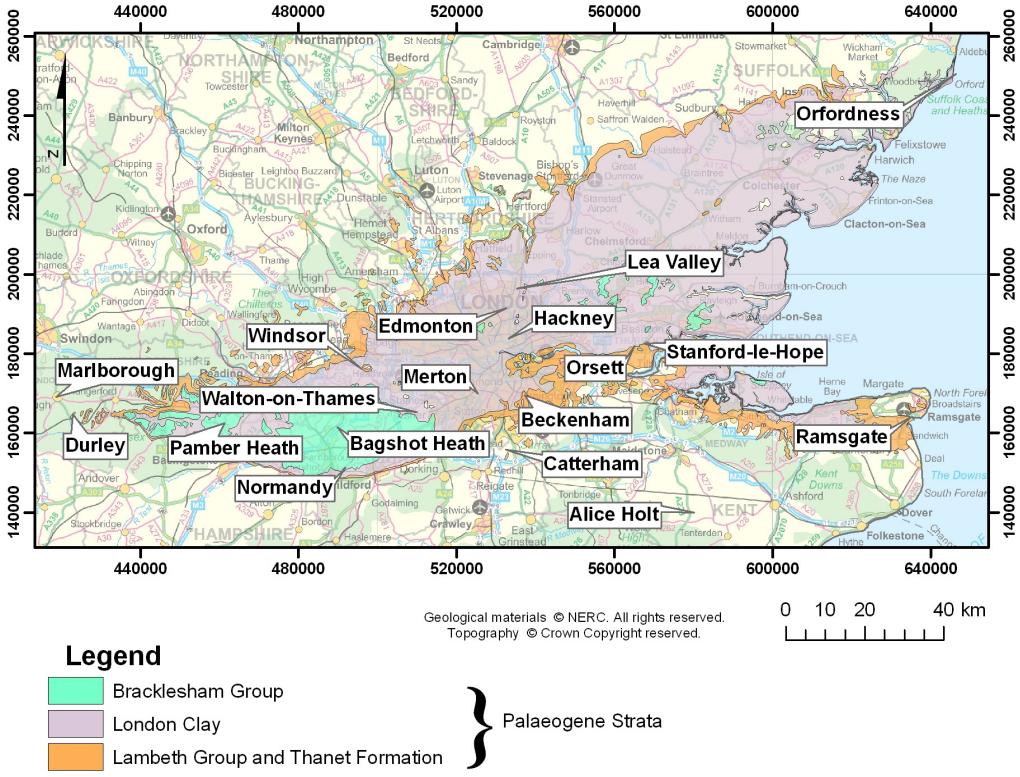

Figure 2.6 Location of minor settlements named in this study

3 Regional geology and hydrogeology

3.1 REGIONAL GEOLOGY

3.1.1 Geological setting

At the start of the Palaeogene the landmass that is now Britain was at approximately 40-50˚N, which is equivalent to that of the central Mediterranean today (McLeish, 1992; King, 2006). The landmass was subject to higher temperatures than experienced in the UK today, and these were further enhanced by a lower temperature gradient between the equator and the North Pole because of the lack of large ice sheets (King, 2006). Britain continued to move northwards, reaching its present latitude (approximately 50-59˚) by the end of the Palaeogene (McLeish, 1992).

Much of Britain had been uplifted at the end of the Cretaceous and deposition was limited to basins in southern England and in the North Sea, extending to East Anglia and the lower reaches of the Thames Basin (McLeish, 1992; Jones et al., 2000). The Palaeogene strata in Britain represent cyclical deposition of shallow marine and coastal sediments laid unconformably on folded Cretaceous Chalk (McLeish, 1992; Ellison et al., 2004). Compression in the late Oligocene to mid-Miocene developed the London Basin, a broad synclinorium (Ellison et al., 2004). As a result of these processes the Palaeogene strata in this area outcrop in a wedge shape covering the lower parts of the Thames Valley and the fringes of the Thames Estuary. A geological map of the area is presented in Figure 3.1 and cross sections in Figure 3.2 and Figure 3.3.

The terminology of Palaeogene strata in the onshore areas of southern Britain has been

Table 3.1 Correlation of Palaeogene strata in the London Basin (adapted from King (2006))

Period	Epoch	Age	Group	Formations in the London Basin	Old Terminology
Palaeogene	Mid Eocene	Lutetian	Bracklesham		
				Camberley Sand Formation	Upper Bagshot/ Barton Beds
				Windlesham Formation	Middle Bagshot/ Bracklesham Beds
				Bagshot Formation	Lower Bagshot Beds/ Sands
	Early Eocene	Ypressian	Thames		
				London Clay Formation	London Clay
				Harwich Formation	London Clay Basement Bed/ Oldhaven Beds
	Late Paleocene	Thanetian	Lambeth	Woolwich and Reading Formations	Woolwich and Reading Beds
				Upnor Formation	Woolwich/ Reading Bottom Bed
				Thanet Formation	Thanet Sands/Beds

formalised relatively recently (see King, 2006 and references herein). In much of the literature the old terminology is used. Table 3.1 presents the correlation of the Palaeogene strata in the London Basin area with the current and old terminology. The new terminology is used in this report.

3.1.2 Thanet Formation

The Thanet Formation is the oldest Palaeogene deposit in the London Basin. The unconformity at its base represents a depositional time gap of ca. 20 million years since the Cretaceous Chalk was deposited (Curry, 1992; Ellison et al., 2004). This formation mainly

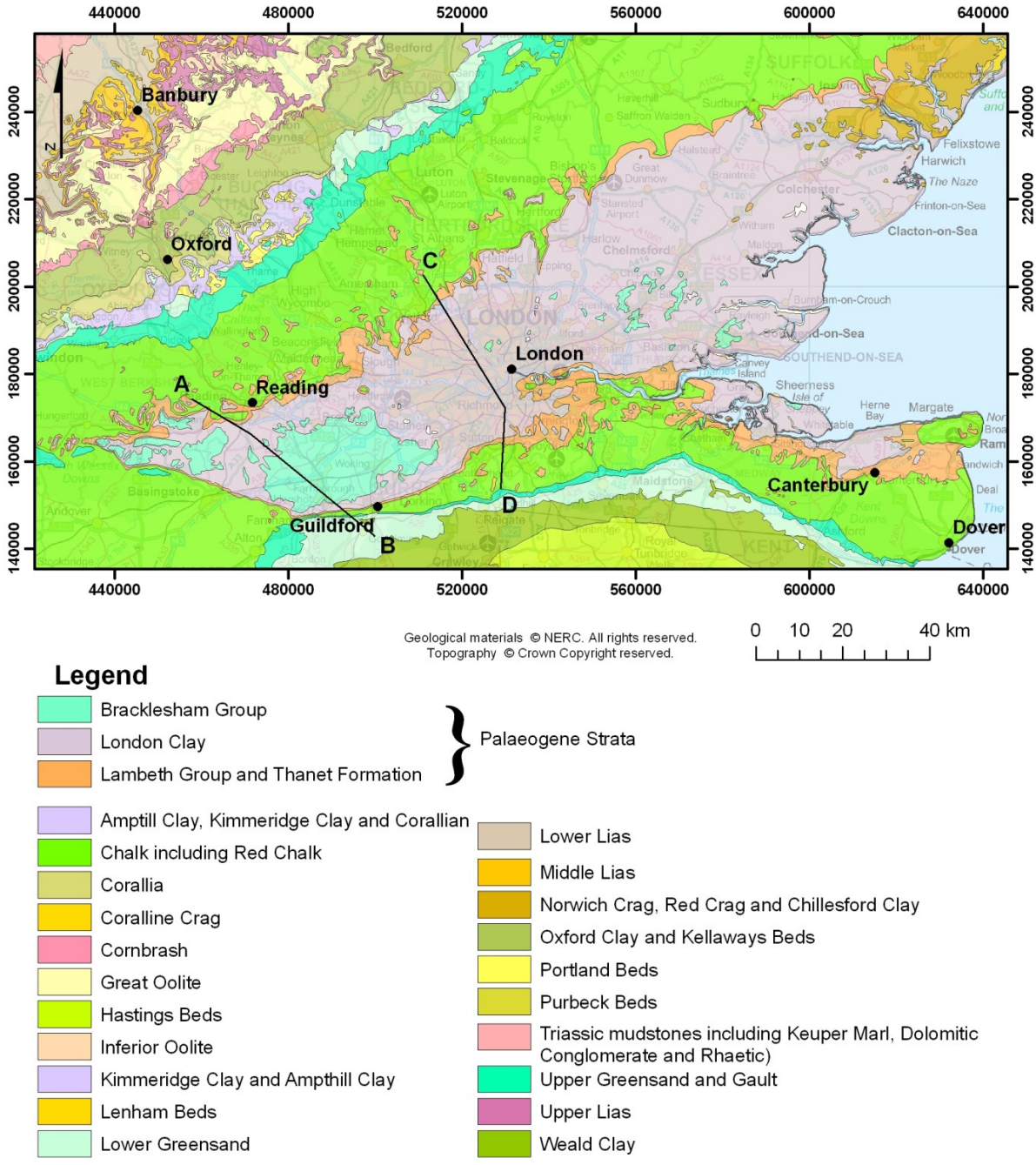

Figure 3.1 Geological map of the London Basin and surrounding area. A-B and C-D indicate lines of cross section (Figure 3.2 and Figure 3.3)

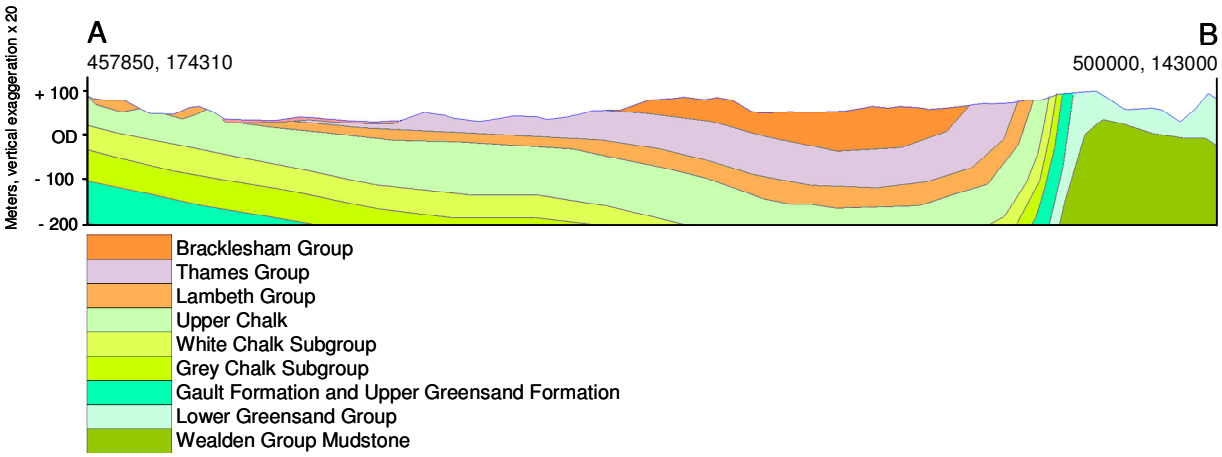

Figure 3.2 Cross section across the Palaeogene outcrop in the Thames Basin, corresponds to A-B line in Figure 3.1

occurs at depth beneath London. The formation outcrops in outliers found around south-east London and Kent. The Thanet Formation is present as a wedge beneath London, which attains a maximum thickness of around 30 m in the region of Stanford-le-Hope [TQ 68 82] and is absent in Guildford and Ipswich (Curry, 1992; Sumbler, 1996; Ellison et al., 2004).

The Bullhead Bed is found at the base of the Thanet formation, developed on a marine erosion surface (Curry, 1992; Ellison et al., 2004). It is a conglomerate containing flint pebbles and nodules within a green-grey glauconitic sandy clay matrix. This unit is found up to 0.5 m thick. The bulk of the Thanet Formation is a coarsening-upwards sequence dominated by silty, fine-grained sand with a clayey and silty base. The colour of the unweathered sands, greenish to brownish grey, is determined by the glauconite content. The sands weather at the surface giving a yellowish grey colour. Primary sedimentary structures are generally lacking as these sediments are extremely bioturbated (Sumbler, 1996; Ellison et al., 2004). The heavy minerals present indicate that the sands are derived from the metamorphic rocks of the Scottish Highlands (Sumbler, 1996).

3.1.3 Lambeth Group

The Lambeth Group has a more extensive distribution than the Thanet Formation and comprises the Upnor Formation and the Woolwich and Reading Formations. The relationships between units within these formations can be very complex especially in central and south-east London. Lambeth Group strata are commonly mapped together. They are generally around 10-15m thick at outcrop, where they are present in narrow tracts around the main Palaeogene mass, and as outliers in the south-east of the area.

The Upnor Formation forms the basal beds of the Lambeth Group, lying unconformably on the Thanet Formation, or, where the Thanet Formation is absent, overlapping onto the Chalk (Ellison et al., 2004). The sediments of the Upnor Formation were laid down in a shallow sea following a period of emergence and erosion. Remarkably, the origin of the sediments is radically different from the Thanet sands, as they originate from the Armorican Province to the south-west, rather than the Scottish Highlands (Sumbler, 1996).

The base of the Upnor Formation is generally well-defined, marked by a bed of rounded flint pebbles (Ellison et al., 2004). Towards the east of the area extensive bioturbation and the

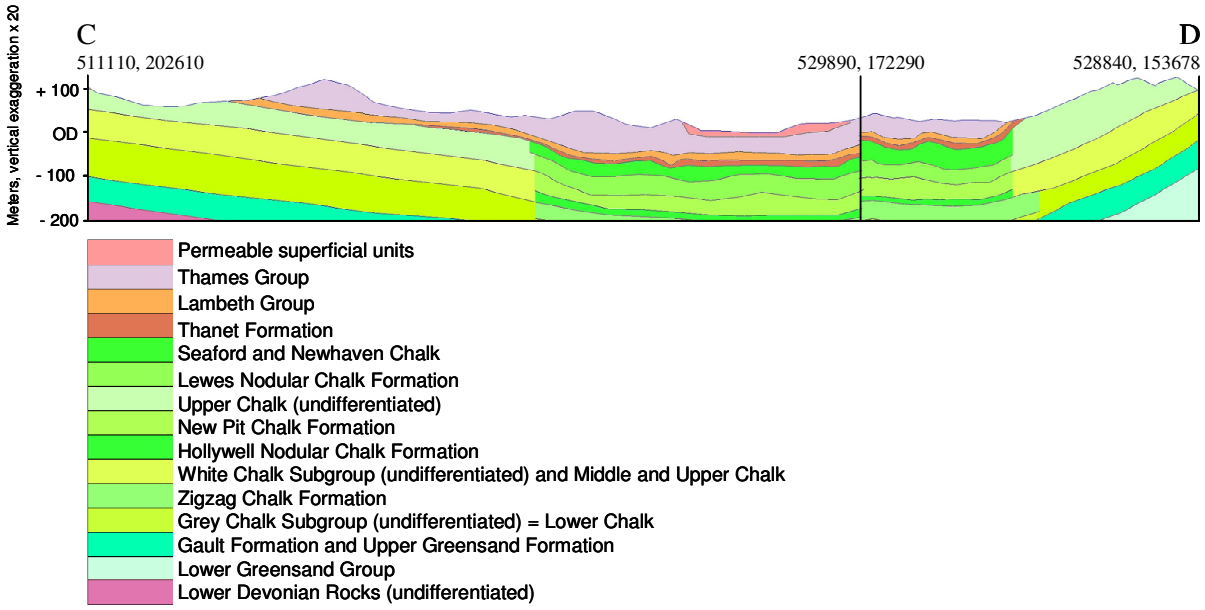

Figure 3.3 Cross section across the Palaeogene outcrop in the Thames Basin, corresponds to C-D line in Figure 3.1. (Seaford and Newhaven Chalk, and Lewes Nodular Chalk Formation are subdivisions of the Upper Chalk; New Pit Chalk Formation and Hollywell Nodular Chalk Formation are subdivisions of the White Chalk Subgroup; and the Zigzag Chalk Formation is a subdivion of the Grey Chalk Subgroup)

absence of the pebble bed has created a gradational boundary between the Thanet Formation and the Upnor Formation (Sumbler, 1996). In the western part of the region, where the Upnor Formation rests directly on the Chalk, the basal bed contains flint nodules, similar to those found at the base of the Thanet Formation. The Upnor Formation is typically composed of fine- to medium-grained sands with varying proportions of glauconite, flint beds, and minor amounts of clay. Where unweathered, the sands are generally dark grey and dark greenish grey, owing to high glauconite content. Where these sediments are weathered at outcrop they are pale grey-brown to orange-brown (Ellison et al., 2004). At Orsett [TQ 64 81] the Upnor Formation includes up to 10 m of coarse gravel of well rounded flint. The flints contain evidence of high-energy conditions and are thought to represent part of an offshore barrier or the infill of a tidal channel (Sumbler, 1996).

After the Upnor Formation had been deposited, a retreat of sea level caused fresh and brackish water to exist over the London Basin. It was at this time that the Woolwich and Reading beds were deposited. These beds are broadly equivalent; the Reading Formation is predominantly found in the north-western areas of the London Basin, while the Woolwich Formation is found around central London and to the south and east of the Greater London area (Sumbler, 1996).

The Reading Formation is either transitional with the Upnor Formation or it rests unconformably on the Thanet Formation or Chalk. This formation is found in the western and northern parts of the Greater London area. In central London, the Reading Formation is divided into the Upper and Lower Mottled Clay, separated by the Woolwich Formation (Sumbler, 1996; Ellison et al., 2004). West of Westminster the formation is generally undivided, but the Upper and Lower Mottled Clays are separated by a lignite bed (Hugget and Knox, 2006). The area where both Upper and Lower Mottled Clay exist extends to Hackney

[TQ 34 84] in the east, Merton [TQ 25 69] in the south and Edmonton [TQ 33 92] in the north. Further east only Lower Mottled clay is present. This is composed of mainly clay in the south and sand in the north. The Reading Formation and the Woolwich Formation interdigitate in central London with the Woolwich Formation resting upon the Lower Mottled Clay (Sumbler, 1996; Ellison et al., 2004).

The Reading Formation is typically 10-15 m thick. It is composed of sediments deposited on marshy mudflats and crossed by river channels. The lithology can vary greatly, but the bulk of the undifferentiated Reading Formation consists of mottled silty clay and clay with sandy units (Ellison et al., 2004; Hugget and Knox, 2006). The colours present are varied depending on soil formation processes and oxidation state of the sediments. They include pale brown and pale grey-blue, dark brown, pale green, red-brown and crimson. The clays are blocky in nature, as a result of numerous fissures. Up to 50% of the unit is present as mottled silt and sand. The colours are mainly brown hues. These beds contain areas of thin laminations and well-sorted sands (Ellison et al., 2004).

The Lower Mottled Clay typically shows purple-red hues. In the upper part of this unit there are irregular shaped carbonate nodules up to 0.5 m in diameter. To the east of Stratford the unit is mainly turquoise-green and brown mottled structureless clayey sand. It contains minor amounts of calcareous clayey sands irregularly iron cemented. The Lower Mottled Clay becomes increasingly sandy towards the east. The Upper Mottled Clay largely consists of mottled clay, silty clay and silt. Its colours are similar to the Lower Mottled Clay, but there are no purple hues (Ellison et al., 2004).

The Woolwich Formation includes a variety of lithologies derived from lagoon or estuarine environments (Sumbler, 1996). It is divided into 3 units: Lower Shelly Clay, Laminated Beds and Upper Shelly Clay. The Lower Shelly Clay sits unconformably on the Lower Mottled Clay of the Reading Formation. The base is sharp and the top of the unit is either sharp or transitional with the laminated beds of the Upper Mottled Clay. Dark grey to black shelly clay dominates this unit, although in east London there is an increase in medium grained sand in the matrix. Some beds are almost entirely composed of shells indicating sediment input was low. In addition there are a few sporadic beds of brownish clay and lignite can commonly be seen at the base of the Lower Shelly Clay (Ellison et al., 2004).

The Laminated Beds typically rest unconformably on the Lower Shelly Clay. The base is either sharp, a rapid gradation from the Lower Shelly Clay, or, in localised areas it interdigitates with the Lower Shelly Clay. These beds consist of thinly interbedded fine- to medium-grained sand, silt and clay with sporadic bivalve shells. Beds are typically <50 mm thick, although localised sand bodies can be up to 5 m thick (Ellison et al., 2004).

The Upper Shelly Clay is mainly found in South London. South-east and north-east of this the Upper Shelly Clay has only been found sporadically in boreholes. The base of the unit is either sharp where it rests unconformably on the Upper Mottled Clay, or a rapid gradation where it rests upon the Laminated Beds. The unit is mainly grey shelly clay with thinly interbedded grey-brown silt and very fine-grained sand. Towards the south-east it becomes mainly sand. Bioturbation and trace fossils are common. In general there is a greater diversity of fauna than in the Lower Shelly Clay (Sumbler, 1996; Ellison et al., 2004).

3.1.4 The Thames Group

The term “Harwich Formation” was introduced by Ellison et al. (1994, cited in Ellison et al., 2004) to include sediments deposited between the Lambeth Group and the London Clay Formation. Hence this term encompasses numerous obsolete informal units. The Harwich Formation was deposited in shallow marine conditions following another rise in sea level. In

South Essex and north Kent the contact is markedly erosive, and cuts down to the Upnor Formation. South of Caterham [TQ 33 55] the Harwich Formation overlies the Chalk. This may not be a true correlation as it is thought Quaternary solifluction processes may be responsible for their transportation (Sumbler, 1996; Ellison et al., 2004).

The Harwich Formation comprises several distinct facies, although it is dominated by fine-grained sand and rounded black flint pebble beds. The proportion of pebbles is varied between units and calcareous, ferruginous and siliceous cements occur locally. In the area centred around Beckenham in south London [TQ 37 69], extending to Lewisham and Croydon, the formation is present as cross-bedded sand with rounded pebbles of black flint. These beds infill channels eroded into the Lambeth Group sediments. North-east of this, in Essex and north Kent, the Harwich Formation is predominantly fine-grained sand and is less pebbly (Sumbler, 1996; Ellison et al., 2004).

The London Clay is the most widespread of the Palaeogene deposits in this area and it forms the majority of the Palaeogene outcrop. The extensive outcrop is only lacking to the south-east of London, where it has been eroded away. The formation has been critical to the development of London's infrastructure. Its homogeneity and structure is ideal for building on and tunnelling within (Sumbler, 1996; Ellison et al., 2004). The London Clay Formation was laid down in entirely marine conditions, and unsurprisingly it is predominantly argillaceous. The London Clay is generally sandier towards the top of the Formation, which consists of relatively homogenous clay. At outcrop the London Clay Formation oxidises to a brown colour which generally extends to around 3-6 m deep, although more permeable sandy layers are oxidised to around 10 m. The London Clay varies in thickness from 90 m at Reading to around 140 m in south Essex and north Kent. Beneath the weathered layer the formation is generally a dark bluish to grey, and characteristically fissured. Pyrite is common throughout as a replacement of fossil shell remains and as small nodules (up to 50 mm) (Sumbler, 1996; Ellison et al., 2004).

The London Clay Formation can be subdivided into five units, of these only the uppermost unit, the Claygate Member, is mapped. The remaining four units are informally denoted A to D. The boundaries between each unit are gradational and are identified by subtle changes in grain-size and glauconite concentration. Each unit is thought to be a sedimentary cycle representing a transgression, followed by a shallowing of the sea (Sumbler, 1996; Ellison et al., 2004).

The lowest unit, Unit A, overlies the Harwich Formation with the exception of areas around central and south London where it lays unconformably on Lambeth Group sediments. A typical cycle commences with a basal bed containing glauconite grains and sometimes rounded flint pebbles, which is succeeded by a sequence of clays becoming more silty and sandy upwards. Although each unit differs slightly in texture, grain size, mineralogy and extent of bioturbation (Sumbler, 1996; Ellison et al., 2004).

The Claygate Member was defined by Bristow et al. (1980, cited in Ellison et al., 2004) as "all the deposits above the base of the lowest fine-grained sandy bed that are thick enough to be distinguished from the underlying relatively homogenous clays [Units A-D]". It can often be difficult to map following this definition as Unit D becomes increasingly sandy and the boundaries are graded. In the central and eastern areas of the London Basin the Claygate Member comprises alternating beds of clayey silt, very silty clay, sandy silt and glauconitic silty fine sand. In comparison to the sandy beds in unit D, the sands in the Claygate Member are coarser-grained and more noticeably glauconitic. In the west of the London Basin the Claygate Member is predominantly a finely-interbedded and thinly-laminated sequence of clay, silt and fine-grained sand. It contains many interbeds of fine-grained, finely-laminated

sands (Ellison et al., 2004). It is thought that the Claygate Member is diachronous and deposits in Surrey are of similar age to the top part of Unit D further east (King (1981), cited in Ellison et al., 2004).

3.1.5 The Bracklesham Group

After the final cycle of deposition of London Clay the sea shallowed. The Bagshot Formation was deposited under either shallow-marine or estuarine conditions. The base of this formation is well-defined by a sharp lithological change. The base can commonly be identified by a line of springs and a change in slope too. The main outcrop area is centred on Camberley [SU 87 60] near Bagshot Heath. The Bagshot Formation is dominated by yellow, orange-brown, and ochreous-brown, fine-grained quartz sand, which can be silty locally.Thin beds of pale grey clay are also present. In addition, pebble beds are common towards the base of the formation. Its relationship with the underlying Claygate Member indicates that the Bagshot Formation is diachronous, younging to the east (Sumbler, 1996; Ellison et al., 2004).

The Windlesham Formation, which varies in thickness from 12-30 m, overlies the Bagshot Formation to the south-west of London. The Windlesham Formation sediments are of varied character and include interbedded greenish grey glauconitic sand, yellowish brown sandy clay and pale grey to lilac clay. Cross-bedded and pebble beds are also found in the younger part of the sequence (Sumbler, 1996).

The Camberley Sand Formation contains the youngest beds in the Palaeogene sequence in the London Basin. They are restricted to the Chobham and Bagshot areas of Surrey. They are characterised by yellowish-brown, fine-grained sands. The deposit is locally glauconitic in the lowest parts with silt beds and clay partings. The formation can be up to 70 m thick but the full sequence is not preserved owing to erosion. At the base of the formation an incomplete bed of up to 3.5 m of rounded flint and chert pebbles occurs. The presence of chert indicates that the Lower Greensand had been uncovered by denudation (Sumbler, 1996; Ellison et al., 2004).

3.2 REGIONAL HYDROGEOLOGY

3.2.1 Aquifer properties

Within the Palaeogene strata there are a number of regionally significant minor aquifers (see Table 3.2). A great lateral and vertical variation within the more argillaceous units can give rise to localised aquifers where lenses of sand are present. The varied nature also gives rise to numerous perched water tables (Jones et al., 2000).

Local groundwater flow is hard to predict within the Palaeogene strata owing to the great variation, particularly laterally. The regional groundwater flow pattern in the London Basin Syncline is from the edge towards the centre. The flow within the Palaeogene is largely controlled by the lithology, e.g. intergranular flow, rather than along fault lines, which have local effects only. The permeability can be increased by weathering caused by percolation of oxidised groundwater (Jones et al., 2000).

Hydrologically the Palaeogene beds can be divided into two groups, divided by the London Clay. The Thanet, Woolwich and Reading, and Harwich formations are commonly considered as a single groundwater unit, and are in hydraulic continuity with the chalk. They have been be referred to as the “Lower London Tertiaries” or the “Basal Sands” aquifer. More specifically the Basal Sands aquifer is defined as “the beds composed of sand or coarser-grade material lying between the top of the Chalk and the first major overlying clay horizon (Water Resources Board 1972, cited in Kinniburgh et al., 1994). Above the London Clay the

Table 3.2 Formations that act as minor aquifers in the London Basin (adapted from Jones et al., 2000)

Formation	Thickness (m)	Distribution	Lithology	Comments
Camberley Sand Formation	up to 70	West of London	Well-sorted medium-grained sand	
Bagshot Formation	up to 27 in Essex outliers and up to 40 m west of London	Outliers in north London and Essex; Surrey and Berkshire	Mainly fine- to medium-grained sand with thin beds of clay and clayey silt	
Harwich Formation	up to 12	South-east and north-east London and north Kent	Well-sorted, fine to medium sand with flint pebble beds	May be in hydraulic continuity with Upnor Formation
Woolwich Formation	10	Mainly central and east London and north Kent	Shelley clay, laminated beds with sand channels 2 to 4 m thick in central London	
Reading Formation	25	Central London and to the west	Highly variable; mottled clay and silt. Fine- to medium-grained sand in layers and channels may constitute up to 60%	
Upnor Formation	up to 10	Entire area	Glauconitic sand with thin clay seams	May be in hydraulic continuity with Thanet Formation
Thanet Formation	up to 32	East of Harrow to Hounslow	Coarsening-upwards silty, fine sand: clay beds at depth in east	

formations which make up the unconfined Bracklesham Group may be considered together as a sandy aquifer above the London Clay, although the Bagshot Formation is the most productive of the late Early to Mid Eocene strata (Jones et al., 2000).

The unconsolidated nature of most of the Palaeogene strata means it is difficult to measure the permeability. The data available are therefore limited, and the hydraulic conductivity (K) was estimated by the Water Resources Board (1972, cited in Jones et al., 2000) for the Basal Sands based on grain-size distribution. The Thanet Sands have an average K of 2.5 m/d, the Woolwich and Reading formations K varies between 2 and 60 m/d, and the Harwich Formation K varies between 2 and 70 m/d. In areas where there is gravel, the Upnor Formation may have a K as high as 200 m/d, but such layers are uncommon and would have little effect on the overall hydraulic conductivity. While the London Clay is not considered a productive aquifer, it is highly fissured in places giving an average K of 10^{-3} m/day. This can be much higher where fissures are particularly common (Downing et al., 1972; Jones et al., 2000). The varied nature of these beds is not only evident vertically, but lateral variations in the Lambeth group can mean sands become less productive laterally, and develop into aquitards (Morris and Cunningham, 2008).

Jones et al. (2000) summarised the values for the Palaeogene in the London Basin as ranging from 10 to 522 m^2/d on the basis of 11 available transmissivity records. Six values of storage co-efficient showed a range of 0.0001 to 0.06. Thirty five values of specific capacity were available giving a range of 2.4 to 469 m^3/d/m.

The Base Flow Index (BFI) can be used as an indication of the proportion of a river's runoff that is derived from stored (groundwater) sources (Marsh and Hannaford, 2008; Bloomfield et al., 2009). The BFI increases with permeability of the bedrock, superficial deposits and soils in a catchment. A high BFI indicates the dominance of baseflow, which will sustain the river's flow during dry periods. Figure 3.4 shows the BFI variation around the London Basin. The rivers are mostly sourced in the Chalk and drain into the centre of the London Basin Syncline. The BFIs are presented only for reaches of river that flow over the Palaeogene strata. In general the groundwater influence is greater (higher BFIs) over the predominantly sandy groups, and lower over clay. While it is unsurprising that the lowest BFIs are found over the London Clay, as it is generally considered an aquiclude, the BFI can be as high as 0.59. This could either be attributed to localised sandy deposits (Ellison et al., 2004) or an increased permeability due to weathering of shallow strata (Lake and Wilson, 1990). In addition the BFIs decrease towards the north-east, which has significant Quaternary cover. See Bloomfield et al. (2009) for more information regarding BFI in the Thames Basin.

3.2.2 Aquifer resources

HISTORICAL GROUNDWATER ABSTRACTION AND RECHARGE

Groundwater has been developed beneath London from the Thanet Formation, Lambeth Group and Chalk since the 18th century. Abstraction from the Palaeogene beds was common

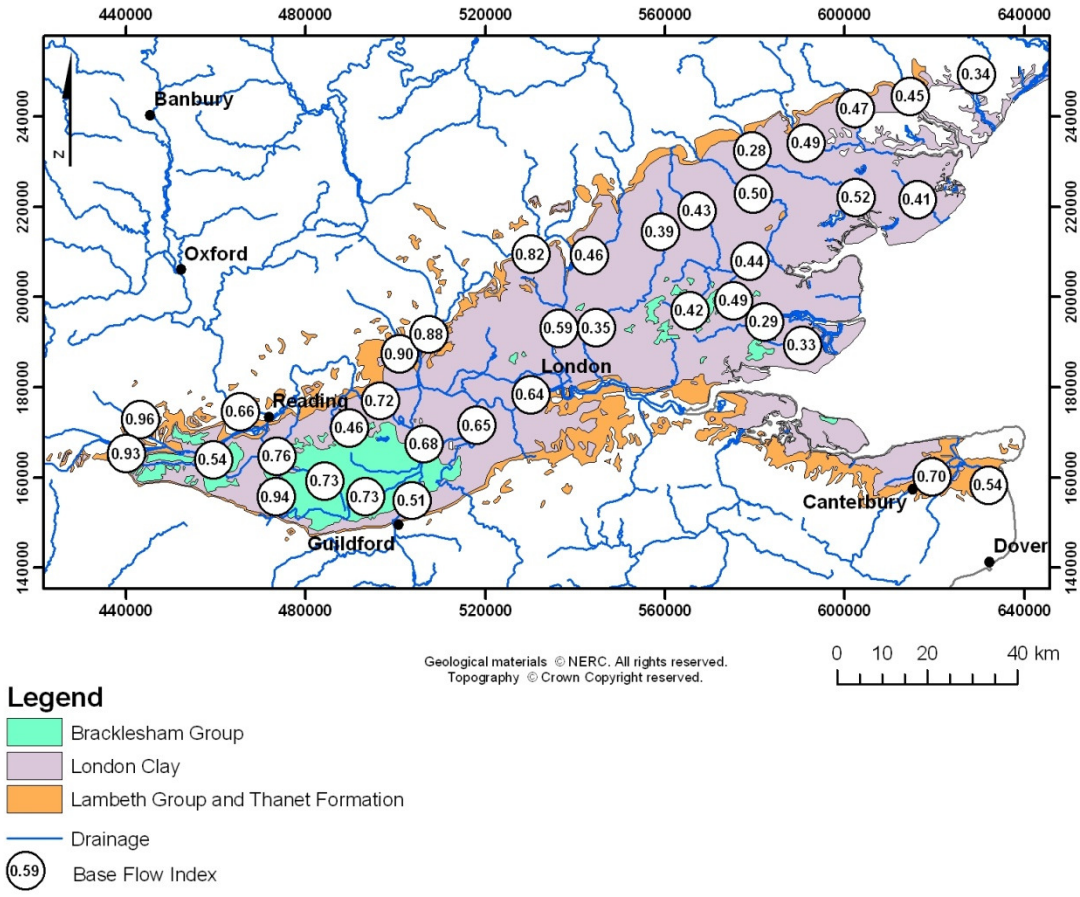

Figure 3.4 The base flow indices of the London Basin River network. Base flow data obtained from Marsh and Hannaford (2008).

in the 19th century, but by the early 20th century, deep boreholes into the Chalk were preferred. Originally water in the Palaeogene and Chalk aquifers was confined by the London Clay or Clays within the Palaeogene strata. Increasing abstraction meant that the Basal Sands dewatered and wells were subsequently deepened into the Chalk. The sands still remained important for distributing groundwater around the basin. Dewatering continued to such an extent that the water level fell below the top of the Chalk in the northern and central parts of the London Basin and water levels declined by up to 75 m (Downing et al., 1972; Jones et al., 2000; Preene and Roberts, 2002; Ellison et al., 2004; Harris et al., 2005; Jones et al., 2005).

The Water Act of 1945 caused groundwater abstraction to be controlled by a licensing system, which meant abstraction has declined and the water level has subsequently risen. In most places within the London Basin the Palaeogene strata are water-bearing and mostly fully saturated (Downing et al., 1972; Jones et al., 2000; Preene and Roberts, 2002; Ellison et al., 2004). This caused additional problems, as much of London's underground infrastructure was developed during the period of declining water levels (Jones et al., 2005)

Artificial recharge, the process of adding treated mains water into aquifers for storage and later use, has been trialled in the London area as early as 1890. Besides the effectiveness of the process, the effect of artificial recharge on groundwater quality had to be considered. A desk study in 1960 identified 4 areas suitable for artificial recharge (Flavin and Joseph, 1983). In 1972 a pilot experiment was carried out at two sites in the Lea Valley. It proved impossible to predict the effects of artificial recharge on groundwater quality over a regional scale, so a prototype scheme was carried out intermittently between 1977 and 1980 (Flavin and Joseph, 1983; O'Shea et al., 1995). Modelling by Gale et al. (1991) suggested that oxidation of FeS_2 in the Palaeogene sands by atmospheric O_2 could generate increased concentrations of SO_4 and Fe (see Box 3.1), although the effects were likely to be localised.

In the 1990s Thames Water developed the North London Artificial Recharge Scheme (NLARS), and further developed with the South London Artificial Recharge Scheme in 2005-2008. Thames Water is responsible for meeting seasonal peak demands, while ensuring underground infrastructure is not affected and abstraction remains sustainable (Harris et al., 2005; Jones et al., 2005). While one of the drawbacks of artificial recharge is considered to be the potential for developing poor water quality (Gale et al., 1991), recent trials have suggested that water quality would improve with continued recharge-abstraction cycles (Kinniburgh et al., 1994; Abesser et al., 2007).

CURRENT RESOURCES

Above the London Clay, the Bagshot Formation and the Camberley Sand Formation are exploited. The Bagshot Formation has a small quantity of good-quality soft water, but this can be limited by fine silt which is easily removed from the formation. Springs can occur around the junction with the underlying London Clays. The Bagshot Formation has a moderately low matrix permeability, but high effective porosity and storage. These properties give rise to reliable yields, and have minimal effects on surface water flow. The aquifer is considered to be underused, but careful planning would be required to avoid siltation (Jones et al., 2000).

The Camberley Sand Formation gives rise to limited groundwater supplies, and is considered secondary to the Bagshot Formation. The water is commonly soft, but ferruginous. Springs occur at the junction with the Windlesham Formation (Jones et al., 2000).

3.3 AQUIFER MINERALOGY AND CHEMISTRY

The varied nature of the deposits means that the mineralogy and chemistry have significant short-range variability. The predominant mineralogy is described here.

The Thanet Formation is a clayey sand where the sand-sized particles are almost exclusively composed of quartz (Ellison et al., 2004). The clay-sized fraction is predominantly smectite with minor illite, and rare kaolinite, vermiculite, and chlorite (Hugget and Knox, 2006). The Bullhead Bed, at the base of the Thanet Formation contains flint pebbles and glauconite coatings. Additional glauconite and mica are distributed sparsely throughout the bulk of the Thanet Formation, and rare irregular nodules of <5mm pyrite are found. The pyrite nodules are presumed to have replaced wood fragments (Ellison et al., 2004). The heavy mineral assemblage varies throughout the formation: the lower half is dominated by an epidote-garnet-hornblende assemblage, whereas a more stable suite of predominantly zircon-rutile-tourmaline-garnet dominated the upper part. Variations in mineralogy in the Thanet Formation are thought to be caused by dissolution of unstable minerals by acidic groundwater (Ellison et al., 2004).

In the Upnor Formation, the non-clay minerals are dominated by quartz. There are variable quantities of glauconite, with subordinate alkali feldspar, chert and mica and traces of collophane and calcite. Clay minerals are dominated by smectite with lesser quantities of illite, and, in the younger beds, kaolinite. The Upnor Formation is characterised by abundant stable heavy minerals, dominated by zircon with rutile and tourmaline (Ellison et al., 2004; Hugget and Knox, 2006).

The clay mineral proportion varies greatly within the Reading and Woolwich formations (Hugget and Knox, 2006). The Reading Formation is dominated by smectite and illite with minor kaolinite and chlorite. The Woolwich Formation contains a similar mixed clay assemblage, but with less smectite and greater proportions of illite, kaolinite and chlorite. The colour variation in these formations is attributed to different oxidation and hydration states of Fe minerals, which only constitute a few percent by volume. Yellows are caused by the presence of jarrosite, oranges and browns by goethite, and red are caused by haematite, which is found in very small quantities. The heavy mineral assemblages of the Reading and Woolwich formations are very similar; both dominated by a zircon-rutile-tourmaline suite. There are low, but variable proportions of the less stable epidote-apatite-spessartite-garnet assemblage (Ellison et al., 2004).

The main lithologies of the Harwich Formation are glauconitic sand and flint pebbles. The overlying London Clay Formation is highly varied (Ellison et al., 2004). Kemp and Wagner (2006) reported a range of mineralogical proportions. Quartz is reported to be 20-70%, feldspar (albite and K-feldspar) is <10%, clay minerals comprise 40-80%, carbonate minerals account for <3% and there are traces of gypsum, goethite and pyrite in the London Clay Formation. Pyrite is present at a concentration up to 2.8%. From 16 new sample analyses, Kemp and Wagner (2006) reported an average London Clay assemblage of 38% smectite, 26% illite, 25% kaolinite, and 12% chlorite. The geochemistry of the London Clay Formation concurs with the above mineral assemblages and typically conforms to the following ranges: SiO_2 ca. 50-70%, TiO_2 0.8-1.1%, Al_2O_3 11-23%, Fe_2O_3 5-14%, Mn_3O_4 0.02-0.16%, MgO 0.07-3.3%, CaO 0.5-2.1%, Na_2O 0.1-o.5, K_2O 2.5-3.9, P_2O_5 0.10-0.16, and SO_3 0.3-1.6 (Kemp and Wagner, 2006).

The Bagshot Formation is predominantly composed of quartz sands with subordinate feldspar, white mica, and heavy minerals which are mainly zircon and tourmaline. There are unmapped flint pebbles at the top of this formation. The formation is oxidised throughout and localised iron pans <5mm thick are developed in places (Ellison et al., 2004).

3.4 RAINFALL CHEMISTRY

Rainwater is the source of most groundwater, providing the initial input of solutes (Appelo and Postma, 2007). Rainwater chemistry is dominated by the influence of marine vapour, and resembles strongly diluted seawater containing carbonic acid and a sea salt aerosol with a mixture of HCl, HNO_3, H_2SO_4, and some NH_4 (Kinniburgh and Edmunds, 1986; Drever, 1997; Appelo and Postma, 2007). Much of the UK is proximal to the sea, so terrestrial rainfall here has a higher sea-salt content than the global average. The Cl^- content is used as an indicator of sea-salt composition, which is generally 3.5 – 10 mg L^{-1} in inland UK areas. This figure equates to a seawater solution of 0.02 - 0.05% (Kinniburgh and Edmunds, 1986).

Box 3.1 Pyrite oxidation and its hydrological and hydrochemical consequences

Pyrite is found sporadically throughout the London Palaeogene strata. The oxidative weathering of pyrite by oxygen can be simplified as:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+$$

Pyrite is oxidised in the presence of an oxidising agent and water, generating acid, Fe(III) and SO_4. Under natural conditions incomplete oxidation of pyrite may occur and Fe^{2+} may not oxidise. Waters affected by pyrite oxidation can therefore be of low pH, with high SO_4 and Fe concentrations. The pH may not be low in the presence of neutralising carbonate minerals (Faure, 1998).

The process of pyrite weathering is an entirely natural mineral dissolution process. However, dewatering of the London Palaeogene aquifer since the late 1800s has allowed air into the dewatered part of the aquifer via wells (see Section 3.2.2), and "windows" of thin or absent Clay over several decades. This has allowed pyrite oxidation, which could not have previously occurred at such a rate owing to the scarcity of oxidising agents (Flavin and Joseph, 1983; Rainey and Rosenbaum, 1989; Kinniburgh et al., 1994).

Acidic groundwater can react with other minerals in the aquifer, which can lead to the generation of very hard water with a high mineral content (Rainey and Rosenbaum, 1989). Additionally reaction with carbonates, which are only present locally in the Palaeogene, but abundant in the underlying Chalk can lead to the rapid release of CO_2(aq). Reaction of acidic water of pH 3-4 with the Chalk would be instantaneous and lead to a huge increase in the partial pressure of CO_2 (Kinniburgh et al., 1994). This presents a significant danger.

Acidic waters with a pH of ca. 3-4 were reported to be seeping through London Underground tunnel linings in 1945. A study in 1989 concluded that these waters, which also contained elevated concentrations of Fe, SO_4, Zn, Al and Co, were derived from naturally-occurring mineral deposits. It was concluded that a sandy lens, present in the clayey tunnelling medium was rich in pyrite, and tunnel expansion works and local borehole drilling had increased the oxygen input allowing localised acidic groundwater to form. The presence of gypsum and jarosite, secondary minerals in the pyrite oxidation process, were found to cause cracking and corrosion of tunnels in conjunction with the acidic water (Rainey and Rosenbaum, 1989).

If conditions continue to support the oxidative weathering of pyrite, the process will continue until all the pyrite is eventually leached out of the sediment (Flavin and Joseph, 1983).

Table 3.3 Rainfall chemistry from the Alice Holt monitoring site [TQ 796 401]. The mean annual rainfall at this site is 832 mm y^{-1} The average rainfall composition and volume was calculated from data provided by the Environmental Change Network (ECN) (www.ecn.ac.uk).

Parameter	Units	Average rainfall composition (2008)	Concentrated rainfall composition (3 × enriched by evapotranspiration)
pH		4.9	
SEC	µS cm^{-1}	23	69
Ca	mg L^{-1}	0.32	0.96
Mg	mg L^{-1}	0.2	0.6
Na	mg L^{-1}	1.6	4.8
K	mg L^{-1}	0.1	0.3
Cl	mg L^{-1}	2.55	7.65
SO_4	mg L^{-1}	0.36	1.08
NO_3–N	mg L^{-1}	0.26	1.56*
NH_4–N	mg L^{-1}	0.26	

*Assuming all NH_4-N is oxidised to NO_3-N on infiltration

The composition of rainwater is determined by the source of the water vapour and the ions that are acquired or lost in the atmosphere. For example rainwater is naturally acidic owing to the dissolution of atmospheric CO_2, which forms a weak solution of carbonic acid with an equilibrium pH of around 5.7. Furthermore, before the rain becomes groundwater, it will be modified by various processes in the soil, including the dissolution of dust and gas particles, evapotranspiration, weathering of soil minerals and uptake by vegetation. Indeed the concentrations of trace elements in rainwater are often much higher than is attributable to a seawater influence. These concentrations result from the partial dissolution of particles of terrestrial and industrial origin by acidic rain (Kinniburgh and Edmunds, 1986; Appelo and Postma, 2007).

Throughfall is water that has been collected beneath a vegetation canopy. It is assumed that the solutes present represent rainwater, dry deposition of particle aerosols and atmospheric gases, and elements cycled through the trees, including evapotranspiration enrichment (Stumm and Morgan, 1996; Drever, 1997). Throughfall has been shown to increase the concentrations of most solutes in rainfall. An increase by a factor of between 2 and 3 is typical of canopy-rain and evapotranspiration interactions (Kinniburgh and Edmunds, 1986). Evapotranspiration causes an increase in the concentration of dissolved salts. Simplified models of the concentration processes produce a first approximation indicating that in Europe, recharge waters are typically around three times more concentrated than rainwaters (Appelo and Postma, 2007). This enrichment is therefore considered reasonably representative of the minimum baseline inputs to groundwater (Abesser et al., 2005b).

Where rainwater can readily infiltrate into the aquifer, it may provide an important source of solutes to the groundwater, especially if the concentrations are enriched because of evaporation and canopy-rain interactions (Kinniburgh and Edmunds, 1986). Table 3.3 shows the chemical composition of rainfall in the area from the Alice Holt monitoring site [TQ 796 401], which is located approximately 7 km south-west of Guildford (ECN, 2006). High

concentrations of Na and Cl in the Alice Holt analyses indicate a strong maritime influence. The rainwater analyses from this monitoring site are representative of the western areas of the London Basin.

The Alice Holt rain water is pH 4.9 indicating there are likely to be airborne pollutants present that are capable of further acidification, such as NO_x and SO_x derived from industry and road emissions (Shand et al., 2007). This is unsurprising given that the Greater London area is the biggest megacity in the European Union with a population of almost 14 million people (Ford et al., 2008).

Areas closer to industrial atmospheric sources are likely to have rainfall with higher concentrations of S and N species and to have a lower pH. If it is assumed that all the NH_4 in rainfall oxidises to NO_3 on infiltration to groundwater, baseline concentrations of dissolved NO_3-N derived from rainfall alone are likely to be in the order of 1.6 mg L^{-1}. The pH of recharge may be even lower than that measured in the rainfall owing to the oxidation of NH_4^+ ions to NO_3 which results in the release of H^+ ions and concentration by evapotranspiration. The pH of recharge is typically in the range 3–5 (Smedley and Allen, 2004; Shand et al., 2007).

3.5 CURRENT PRESSURES ON GROUNDWATER QUALITY

The Environment Agency's Water Framework Directive (WFD) River Basin Management Plans for the Thames River Basin District identify the current status of groundwater in the study area. The chemical (quality) status of the groundwater bodies[1] comprising principally of Palaeogene deposits is generally determined to be "good". The groundwater bodies which are at "poor" status are the Late Palaeocene beds located along the northern boundary of the Palaeogene outcrop and the area around Greenwich (EA, 2009).

Despite being at "good" chemical status the groundwaters are monitored to ensure that no deterioration of groundwater quality occurs. The main risk of not achieving the quality objectives in the Thames Basin by 2015 under the Water Framework Directive (WFD) is due to the potential impacts of hazardous substances and other pollutants caused by industrial development and urbanisation. Population, housing and industrial growth can increase the pressures on water quality as pollutants can derive from sewerage leaks, fertilizer and pesticides used on parks and gardens, and run off from roads, drives, car parks, car washing, industry and contaminated land. The responsibility for prevention of pollution is divided between urban, transport, construction and water industries (EA, 2009).

Other pressures on the groundwater quality include the presence of nutrients (nitrate and phosphate) in the drinking water, and the possibility of abstraction causing saline intrusion along the Kent Coast. The groundwater bodies are all classified as drinking-water protected areas, which mean that they need to be managed for this use, and are protected by WFD legislation. In particular, action needs to be taken to limit the inputs of NO_3 to the groundwater to ensure that there is no future deterioration of groundwater quality, and any increasing NO_3 concentration trends can be reversed. Actions to achieve this are by a combination of regulatory and voluntary measures. Nitrate vulnerable zones (NVZs) were first designated by the EA in 1996, and then updated in 2002 and 2008. Currently almost 70% of England is designated as an NVZ. Farms within NVZs have to comply with rules affecting their careful planning, storage and usage of organic and inorganic NO_3 fertilisers. Voluntary measures, such as catchment-sensitive farming (CSF), are also encouraged in order to protect the groundwater from NO_3 contamination.

[1] Groundwater bodies are the management units defined for the purposes of the Water Framework Directive.

4 Data availability and analytical methods

4.1 DATA SOURCES

Groundwater chemical data were acquired for the area by collection of 19 new groundwater samples and collation of available data from past BGS reports (12 sites) and the Environment Agency (EA) database (11 sites). The BGS data are obtained from two sources: Kinniburgh et al. (1994), who describe eight Thanet Formation observation boreholes in the Lea Valley, North London; and Abesser et al. (2007), who studied four Thanet Formation observation boreholes as part of a study to identify potential south London artificial recharge sites (SLARS). The paper by Kinniburgh et al. (1994) includes full analyses of the major elements, selected trace elements, and field-determined parameters; and it also includes major element and selected trace element analyses of pore water taken from the London Clay, Woolwich and Reading Formations and the Thanet Formation. These are discussed separately in Section 5.5. The report by Abesser et al. (2007) includes the full suite of major and trace elements, and field-determined parameters.

The EA data include full analyses of the major elements and selected trace elements and field-determined parameters. These data comprise time series analyses, generally spanning from 2002 to 2009. These time series data are discussed separately in Section 5.6. The most recent EA data and the BGS data from Abesser et al. (2007), and Kinniburgh et al. (1994) were added to the 19 new groundwater samples to expand the spatial coverage, and create a data set of 42 sites (see Figure 2.4).

4.2 SAMPLING AND ANALYSIS

The 19 new groundwater samples were collected by BGS between 7th to 10th September 2009 and 19th to 22nd October 2009 from private boreholes abstracting groundwaters from the Bracklesham Group, Thames group, Lambeth Group and Thanet Formation. The sample locations are shown in Figure 2.4 and Figure 2.5.

Samples were mostly collected from pumping boreholes. Where practical, the pumps at private sources were switched on at least 10 minutes prior to samples being taken. Efforts were made to sample the groundwater as close to the borehole as possible and with minimum transport through pipes or hoses. Sampling from storage tanks was avoided. Where there was no pump or the pump was out of use, a caravan pump was lowered as far as possible, while avoiding the bottom of the borehole or well. In this case the samples were not taken until a stable reading was obtained. It was generally not possible to pump three times the well volume owing to the large bores and small capacity of the caravan pump, although all efforts were made to ensure collection of a representative ground water sample.

At each site, measurements were made of temperature, specific electrical conductance (SEC), alkalinity (by titration against H_2SO_4), pH, dissolved oxygen (DO) and redox potential (Eh). The latter three parameters were measured in an anaerobic flow cell to prevent contact with the atmosphere and parameters were monitored until stable readings were obtained. In a few cases, use of a flow cell was not possible and on-site parameters were measured rapidly in a bucket. In each case a note was made of the sampling conditions.

Groundwater samples were also taken at each site for laboratory analysis. Samples for major- and trace element analysis were collected in factory-new rinsed polyethylene bottles and filtered to <0.2 µm. Filtration was performed using a disposable filter and syringe. Those required for cation and trace element analysis were acidified to 1% (v/v) HNO_3 to prevent metal precipitation and minimise sorption onto the container walls. Aliquots of the sample

filtered to <0.2 µm were also collected in polyethylene bottles preloaded with potassium persulphate for the determination of total dissolved phosphorus (TDP).

Samples for dissolved organic carbon (DOC) analysis were filtered through a 0.45 µm silver-impregnated filter and collected in glass vials pre-cleaned with chromic acid. Samples for the determination of stable isotopes (^{18}O and ^{2}H in water and ^{13}C in dissolved inorganic carbon) were collected unfiltered in rinsed glass bottles.

Analysis of major and trace cations, and I was carried out by inductively-coupled plasma mass spectrometry (ICP-MS). Anions (Cl, NO_3, NO_2, Br and F) were determined by ion chromatography (IC), NH_4 by automated colorimetry (AC), and any titrations repeated in the laboratory were determined by potentiometric titration. Samples for DOC were analysed using a TOC analyser

4.3 DATA HANDLING

The data collected as a result of the sampling campaign and the archive EA data were combined into one set for the purposes of statistical handling and interpretation. For many trace elements, the concentrations were below the detection limits of the analytical techniques used. As the data reported were obtained from more than one laboratory source and by more than one method, the detection limits for any given determinand can vary, indeed detection limits can vary from day to day on a single instrument. This produces left-censored data sets that require special statistical analysis methods for calculating descriptive statistics.

Summary statistics were calculated in the R statistical computer environment (R Development Core Team, 2005) using the NADA package. This package is used to perform statistical analysis on censored data and uses the methods described in Helsel (2005). The methods used to summarise the combined BGS-EA dataset were the Kaplan-Meier (K-M) method and the robust "regression on order statistics" (ROS) method. These methods can both be used to summarise multiply-censored data sets (Lee and Helsel, 2005b, 2007).

The K-M method is commonly used in the medical sciences and is the standard method for estimating summary statistics of survival data. It is also recommended for environmental data (Lee and Helsel, 2007). The K-M method neither needs, nor makes, any assumptions about the distribution of the data, making it suitable for summarising censored data (Helsel, 2005). It only accepts right-censored data but the method can be equally valid for left-censored detection-limit data if they are flipped. The K-M method calculates the rank of the flipped data, placing each non-detect at its detection limit prior to ranking. The method thus accounts for the censored data between the detected observations. The summary statistics are estimated using the empirical cumulative distribution function of the ranked data. Typically this method produces a small positive bias in the mean produced for environmental data. However the method is considered to be suitable for datasets where fewer than 50% of the data are censored (Abesser et al., 2005a; Helsel, 2005).

The ROS method used in the NADA package was originally called the Multiple-limit Regression (MR) method by Helsel and Cohn (1998, cited in Lee and Helsel, 2005b). It is a "robust" semi-parametric method which has been evaluated as one of the most reliable methods for producing summary statistics of multiply-censored data (Shumway et al., 2002). The method is particularly useful for small data sets (n<30) where other methods may become inaccurate. It is also particularly useful where the non-detects comprise up to 80% of the data set. Regression-on-order statistics is a probability-plotting and regression approach that models censored distributions using a linear regression of observed concentrations against their normal quantiles (or "order statistics") (Lee and Helsel, 2005a). The method firstly

computes Weibull-type probability distributions of the data set, which includes both the censored and non-censored data. The formula used is designed to account for multiply-censored data. The plotting positions of the uncensored observations and their normal quantiles define a linear regression. This regression model can then be used to estimate the concentrations of the censored observations as a function of their normal quantiles (Lee and Helsel, 2005a). The last stage in the algorithm is to combine the observed uncensored values with the modelled censored values to produce estimations of the summary statistics. This combination of observed and modelled censored values creates a method that is more resistant to non-normality of errors and also reduces any transform biases that occur (Lee and Helsel, 2005a).

As noted by Lee and Helsel (2005a, b), where the data set has greater than 80% non-detects, the estimated summary statistics are very tenuous. They suggest that in such cases the data can only be summarised by presenting minimum and maximum values (Lee and Helsel, 2005a). The summary statistics in this report were calculated using each of the above methods. The most appropriate method for each analyte was taken following the recommendations of Helsel (2005), as given below:

non-detects <50% of analyte data	K-M method
non-detects between 50% and 80% of analyte data	ROS method
non-detects >80%	ranges only quoted.

The summary statistics reported are therefore derived from a range of methods and do not all present the same parameters. Table 4.1 summarises the statistical parameters that each test can return. To produce the box plots in this report (Figure 5.6 and Figure 5.18), ROS statistics have been applied using functions available in the NADA package.

In the Baseline report series, the 95th percentile of a data distribution has typically been used as an upper cut-off for outlier compositions. The choice of percentile is somewhat arbitrary and other percentiles have been used elsewhere in the literature. The 90–95th percentile was used by Lee and Helsel (2005a) and the 97.7th percentile was used by Langmuir (1997). While using percentiles as an upper limit provides a simple definition of outliers, the method clearly has its limitations. For example, many UK groundwaters are contaminated by nitrate derived from long-term use of nitrogenous fertilisers in agriculture. Nitrate concentrations are therefore variable and the 95% threshold in unconfined aquifers rarely represents a cut-off between natural and anthropogenically-influenced compositions. Likewise, for some

Table 4.1 Summary statistical parameters returned by the methods used in this study. (K-M is the Kaplan-Meier method and ROS is "regression-on-order statistics"; see text for details)

Method	n*	n(c)*	Minimum	Mean	Maximum	0th percentile	25th percentile	50th percentile	75th percentile	90th percentile	95th percentile	100th percentile
K-M	✓	✓	✓	✓	✓	×	✓	✓	✓	✓	✓	×
ROS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Ranges only	✓	✓	✓	×	✓	×	×	×	×	×	×	×

*n denotes number of samples and n(c) denotes number of censored samples

elements, data presented above a given threshold are presented as anomalous, when they can in fact represent baseline concentrations. However, the 95th percentile represents a simplification to exclude the upper 5% of the data distribution and has been used in the Baseline report series as one measure for estimating likely upper limits to baseline concentrations. Concentrations above this threshold are unlikely to be exceeded in future samples unless conditions within the aquifer have changed. It should be emphasised that this is not the only factor used when attempting to characterise the baseline groundwater compositions. A combination of understanding of the hydrogeological and geochemical processes, rainfall compositions, land use and residence times, together with temporal variability observed through time-series data are also taken into consideration. These are discussed later in Section 5.

In addition to the statistical analysis, saturation indices were calculated for the newly collected groundwater samples using PHREEQCi with the `wateq4f.dat` database. Saturation indices will be discussed where appropriate in Section 5.

5 Regional hydrochemistry

Sandstones can form good aquifers, for example the Permo-Triassic sandstones are the second most productive UK aquifer, forming around 25% of the total UK licensed abstractions (Allen et al., 1997). Despite moderately high intergranular permeability the Palaeogene of the London Basin is a relatively minor aquifer owing to a low productivity. This low productivity is a result of a limited saturated thickness, a strong anisotropy as a result of silt and clay interbedding, and rapid changes in thickness and facies caused by the shallow marine depositional environment (Jones et al., 2000). The Thames Palaeogene data set is discussed below in terms of data distribution (i.e. summary statistics of the spread of data), as well as spatial distribution. The spatial distribution is mostly controlled by depth of sample, and hence geological unit intercepted (see Figure 2.5). Data obtained from the Lambeth Group and Thames Group are limited (one site each), so caution is taken when interpreting these results not to place significance on these sites which alone cannot be used to define the baseline concentrations for these groups.

5.1 MAJOR CONSTITUENTS

Statistical data for major ions, field-determined parameters and stable isotopes are summarised in Table 5.1, Figure 5.1, Figure 5.6, and Figure 5.7. In addition spatial variations are presented in Figure 5.2 to Figure 5.5 and Figure 5.8 to Figure 5.17. It must be noted that

Table 5.1 Statistical summary of field-determined parameters, major ions, stable isotope compositions, and nitrogen species

	units	n	n(c)	min	mean	max	P0	P5	P25	P50	P75	P90	P95
Temp	ºC	36	0	8.35	12.4	15.4		10.3	11.8	12.4	12.9	14.3	15.2
pH		42	0	4.65	6.78	11.1		5.09	6.31	6.68	7.34	7.7	7.84
Eh	mV	25	0	-59	237	471	-59	37.6	132	201	375	420	434
DO	mg/L	35	0	0.05	3.36	9.99		0.06	0.17	2.6	5.19	8.45	9.36
SEC	µs/cm	42	0	131	787	3290		215	352	477	1020	1650	2370
δ^2H	‰	23	0	-55.1	-46.4	-40.9	-55.1	-52.4	-48.3	-46	-43.9	-42.3	-41.3
$\delta^{18}O$	‰	23	0	-8.01	-7.14	-6.64	-8.01	-7.79	-7.33	-7.11	-6.85	-6.69	-6.64
$\delta^{13}C$	‰	23	0	-19.7	-16.5	-6.81	-19.7	-19.7	-18.7	-17.1	-14.9	-14.2	-12.3
Ca	mg/L	42	0	6.7	84.6	415		9.5	18.2	42.6	115	167	366
Mg	mg/L	42	0	0.181	20.4	165		3.21	5.36	8.54	19.8	35.4	51.1
Na	mg/L	42	0	8.7	43.1	340		9.8	11.4	20.1	41.1	115	141
K	mg/L	42	0	1.2	12.9	105		2.33	3.93	6.5	12.1	28.3	42.6
Cl	mg/L	42	0	13.4	55.1	283		14	22.7	38.3	57	84.5	188
SO_4	mg/L	42	0	0.215218	184	1830		10.9	36	72	146	292	527
HCO_3	mg/L	41	0	5.4864	171	596		12.2	59.7	137	261	337	404
NO_3-N	mg/L	42	22	<0.02	4.76	55.7	0.000219	0.00055	0.00656	0.0548	0.357	18.1	34
NO_2-N	mg/L	42	29	$<6\times10^{-4}$	0.0174	0.347	9.03×10^{-5}	1.96×10^{-4}	0.000721	0.00232	0.0124	0.0225	0.0487
NH_4-N	Mg/L	42	9	<0.01	0.33	6.7		0.006	0.02	0.069	0.19	0.73	0.94
DOC	mg/L	30	0	0.3536	3.52	45.3		0.37	0.68	1.34	2.27	5.11	12.4
Si	mg/L	42	0	0.5	9.74	27.5		2.44	4.7	7.67	11.4	21.4	25.3

DO: dissolved oxygen; SEC: specific electrical conductance; DOC: dissolved organic carbon; P: percentile; n(c): number censored; min and max are observed values

where an element or parameter was not included in the either the EA or Kinniburgh et al. (1994) data sets only data for the 19 new BGS sites and four sites from Abesser et al. (2007) are presented.

The sand and clay dominance of the Palaeogene beds mean the hardness of the waters is generally low, although some hard waters are present. The Palaeogene aquifers are largely composed of quartz, but the reaction of silica minerals is minor compared to carbonate dissolution. When calcium carbonate minerals are present in rocks and soils at a level of 1% or more they will tend to dominate the aqueous chemistry (Hem, 1992; Langmuir, 1997; Faure, 1998). Table 5.1 and Figure 5.1 demonstrate the dominance of Ca, indicating the presence of Ca minerals as either grain coatings or cement. Figure 5.1 demonstrates that, while the data are varied, most samples are Ca-HCO_3 to Ca-SO_4 type. Only one sample stands out from this general trend, the only sample from the Lambeth group is a Na+K-Cl-HCO_3 type. There is no convincing distinction between the samples taken from the Bracklesham Group and those from the Thanet Formation, and there are too few data points to draw conclusions from the distribution of the water types in the Thames Group and the Lambeth Group. Baseline data for the Palaeogene strata in the Wessex Basin showed that groundwaters sampled from boreholes which penetrated the London Clay Formation tended towards Na dominance (Neumann et al., 2004).

The temperature of the groundwaters ranges from 8.35 to 15.4˚C, with a 5th to 95th percentile range of 10.3-15.2˚C, and a median of 12.4˚C (Table 5.1). Temperature can be used as an

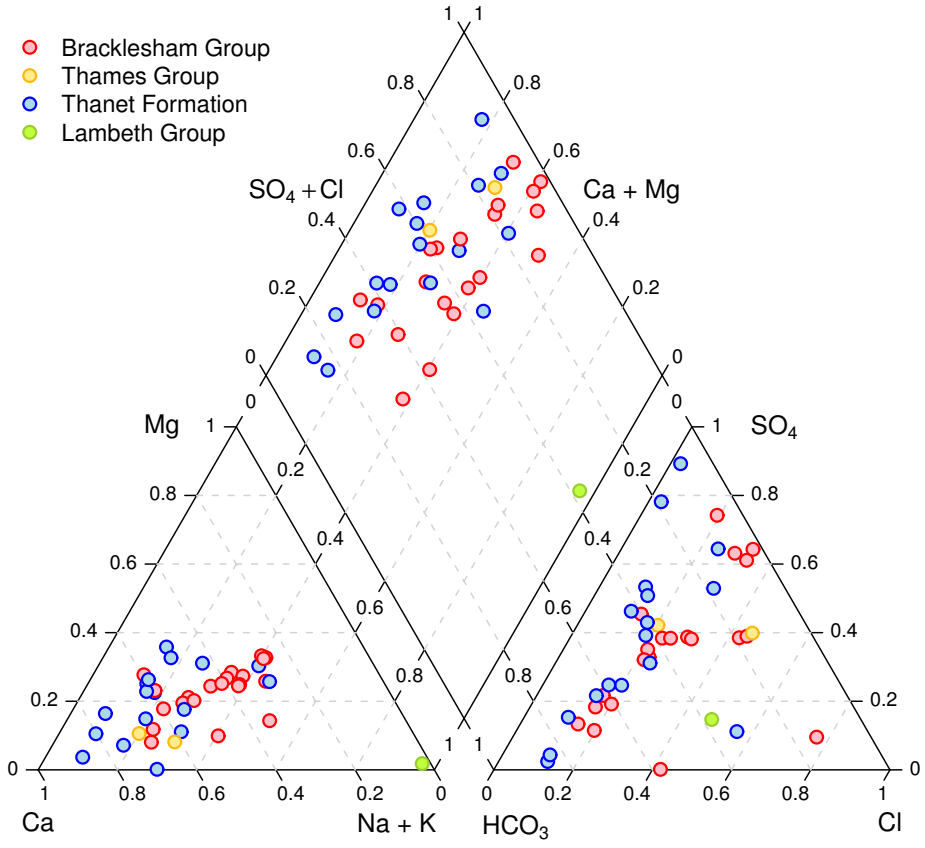

Figure 5.1 Piper diagram of London Palaeogene groundwaters

indicator of depth, due to the geothermal gradient, and in turn this can be used as a proxy to indicate residence time. The temperatures recorded in this study do not show spatial trends (Figure 5.2), nor do they correlate to the formation from which they were abstracted (Figure 2.5). However the depth of most of the samples is uncertain. The temperatures of most samples are up to 5˚C warmer than average surface water temperatures (ECN, 2006).

The pH values range from 4.65 to 11.1, which is a very large range. The majority of the pH data i.e. the 5th to the 95th percentile ranges from 5.09 to 7.84, indicating circum-neutral to weakly acidic waters. The maximum value was thought to be caused by contamination of backfilled cement in the borehole (Abesser et al., 2007). The sample was nonetheless retained in the data set because the cause of the high pH value is not certain, but it may provide an insight into urban construction contamination. The arenacous – argillaceous nature of the aquifer means there is little to moderate buffering capacity. The spatial distribution of pH values (Figure 5.3) seems to indicate a geological control as the higher pH values are measured in samples taken from the Thanet Formation, whereas the more acidic values are measured in samples taken from the Bracklesham Group, Thames Group, and Lambeth Group (see Figure 2.5). It is likely that this distribution is either due to the presence of pyrite in the Bracklesham Group (this is discussed further in Section 5.2.5 and Box 3.1), a distribution of minor carbonate minerals linked to the geology, or a combination of both. The highest pH value was measured in a ground water from the Thanet Formation, it does not affect this general trend.

The range of measured dissolved oxygen is large, with measurements ranging from 0.05 to 9.9 mg L^{-1}. This is a complete range from anoxic to fully saturated. There is a similarly large 5th to 95th percentile range of 0.06-9.36 mg L^{-1}. The redox potential likewise ranges from -59 to 471 mV, and the 5th to 95th percentile range is 37.6-434 mV. These represent a large variation in the redox status of the sampled waters. The most oxidised waters occur to the south of the region (Figure 5.4), although there is little correlation with the source formations (see Figure 2.5). It seems likely that the redox potential is determined by localised

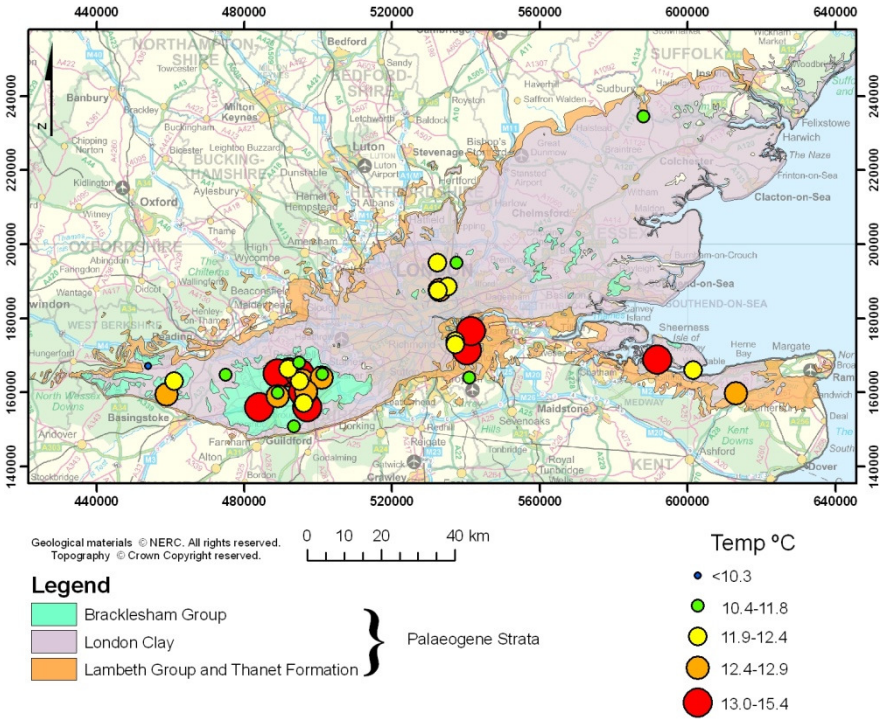

Figure 5.2 Regional variation of temperature within the London Palaeogene aquifer

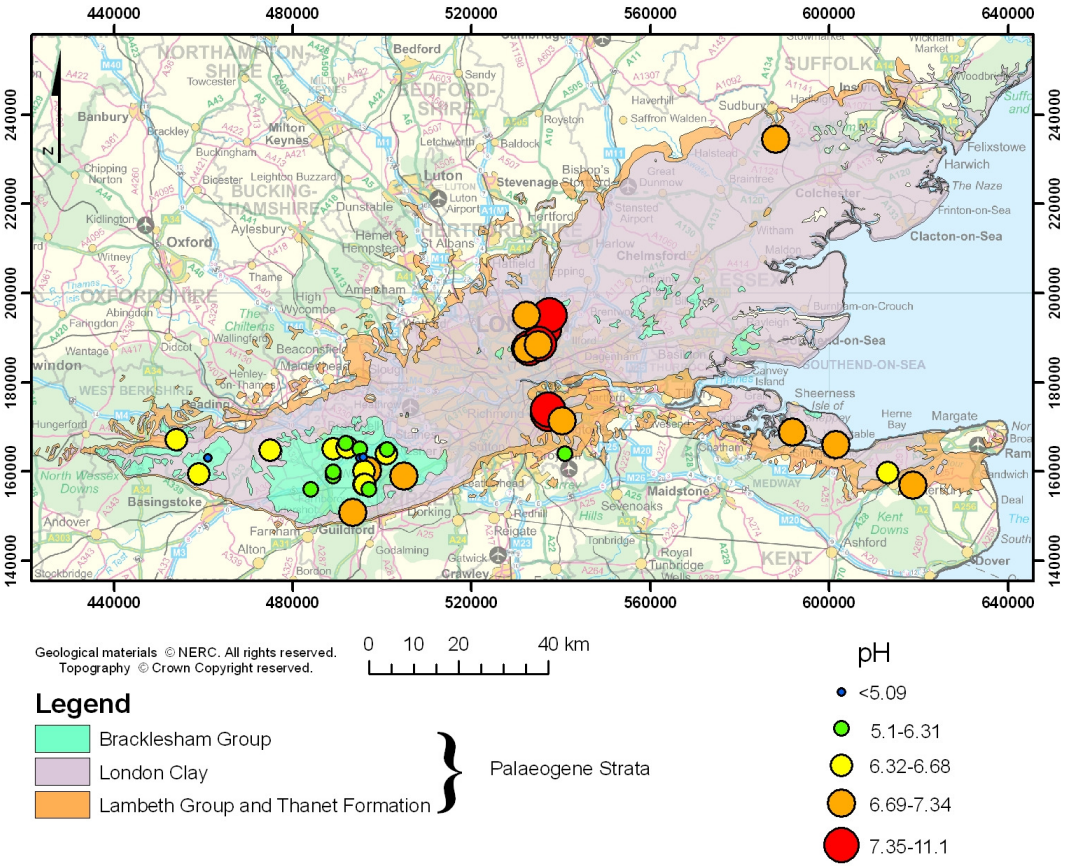

Figure 5.3 Regional variation of pH within the London Palaeogene aquifer

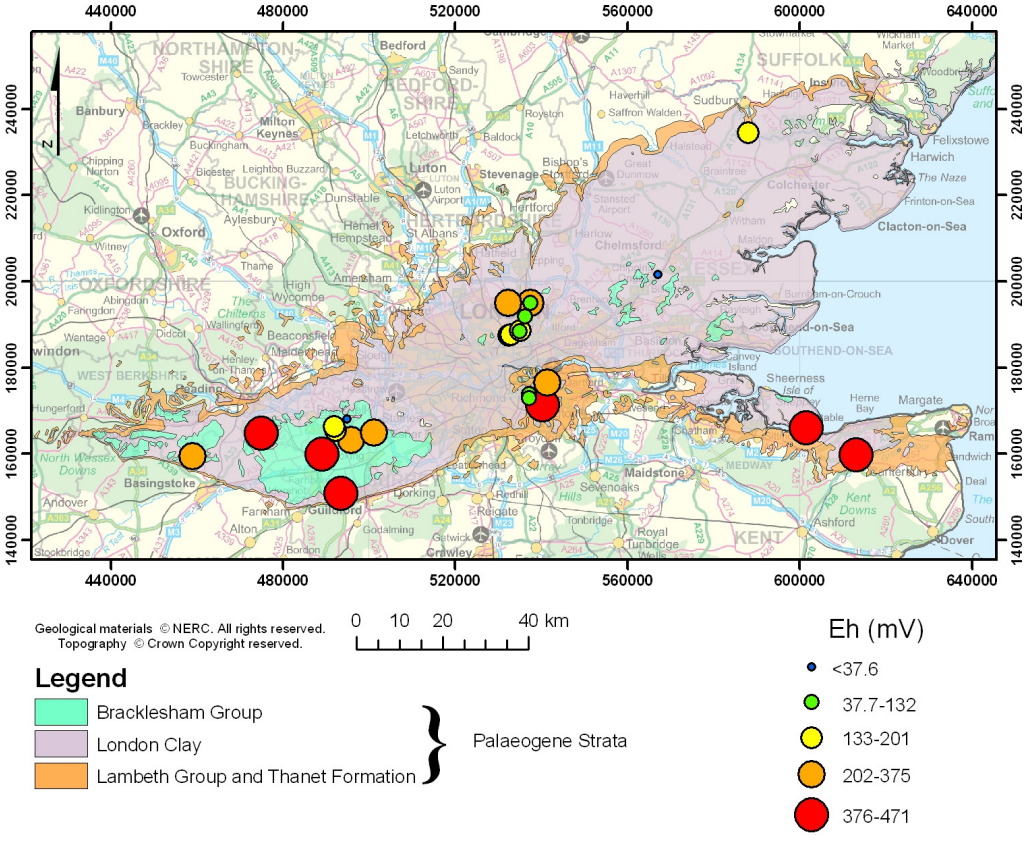

Figure 5.4 Regional variation of Eh within the London Palaeogene aquifer

conditions in the source formation. The interdependence of pH and Eh are the critical factors determining the stability of minerals present, and controlling solubility and speciation (Levinson, 1974). This will be discussed where relevant when discussing elemental concentrations.

The range in specific electrical conductance (SEC) is also large, spanning from 131 to 3,290 µS cm^{-1}. The 5th to 95th percentile range is 215 to 2370 µS cm^{-1}. While the lower values may represent recently recharged groundwater, the arenacous to argillaceous aquifer is dominated by minerals with slow reaction kinetics (after Shand et al., 2007), meaning dissolution may be slow and provides limited loads of solutes to the groundwater. The lowest concentrations are found in the Bracklesham Group groundwaters, and the highest concentrations are found in the Thanet Formation groundwaters (Figure 5.5). This correlation to the geological formations is quite striking, and the elemental concentrations are needed to interpret the SEC distribution.

The major-ion data are presented as cumulative probability distribution plots on Figure 5.7 and as box plots in Figure 5.6. Both provide a useful graphical method for summarising and characterising geochemical data distributions (Shand et al., 2007). These plots are used here to present the range of results from the combined data sets comprising the new BGS data, the previous BGS data and the EA data sets.

Box plots are used to show data ranges of a population and identify outliers. They are hence very useful indicators of baseline ranges. A complete explanation is provided in Section 4.3. Cumulative probability plots are an efficient way of identifying distinct populations and defining anomalies. If the x axis (concentration) is logarithmic, a log normal distribution will plot as a straight line, and bimodal, or multimodal distributions will plot as curves (see Shand

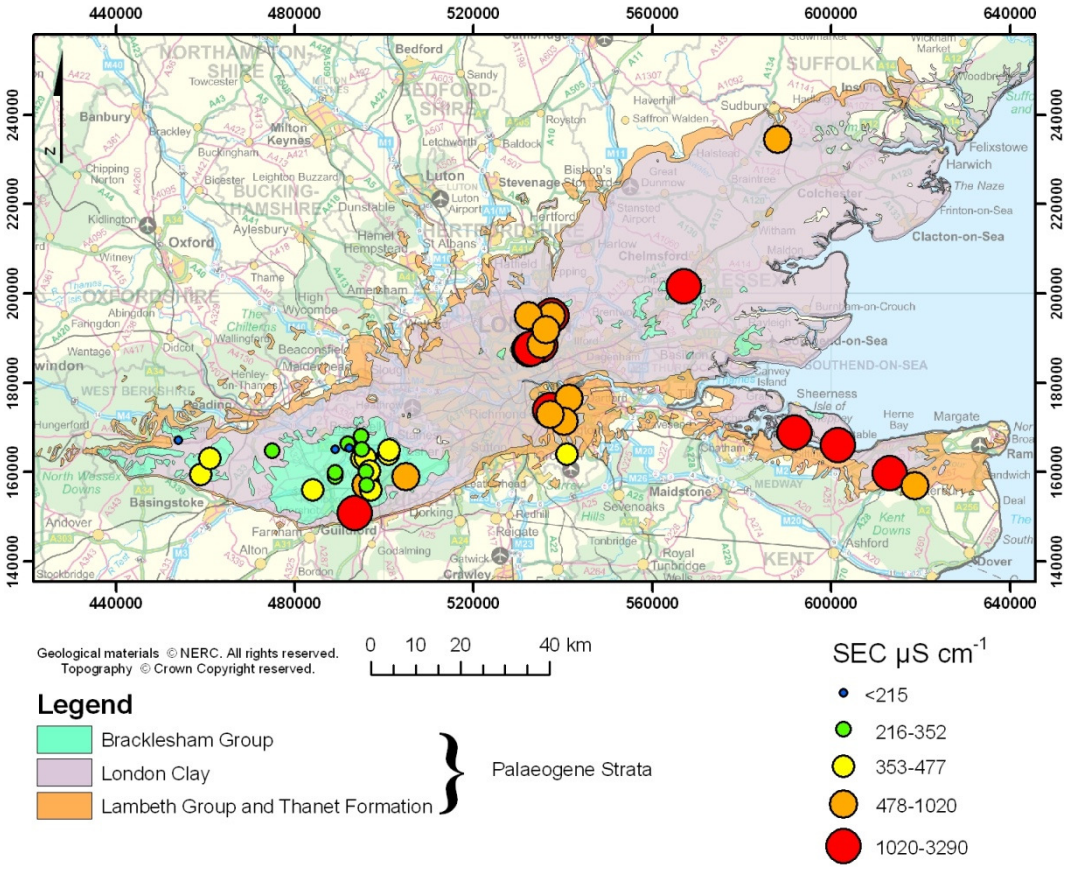

Figure 5.5 Regional variation of SEC within the London Palaeogene aquifer

et al., 2007 for more details). In cumulative-probability plots, flexure may be used to discriminate baseline concentrations from anomalous populations. However, when interpreting cumulative-probability plots, care must be taken as natural reactions, such as redox reactions, sorption and denitrification can introduce anomalous concentrations, which are of entirely natural origin (Shand et al., 2007).

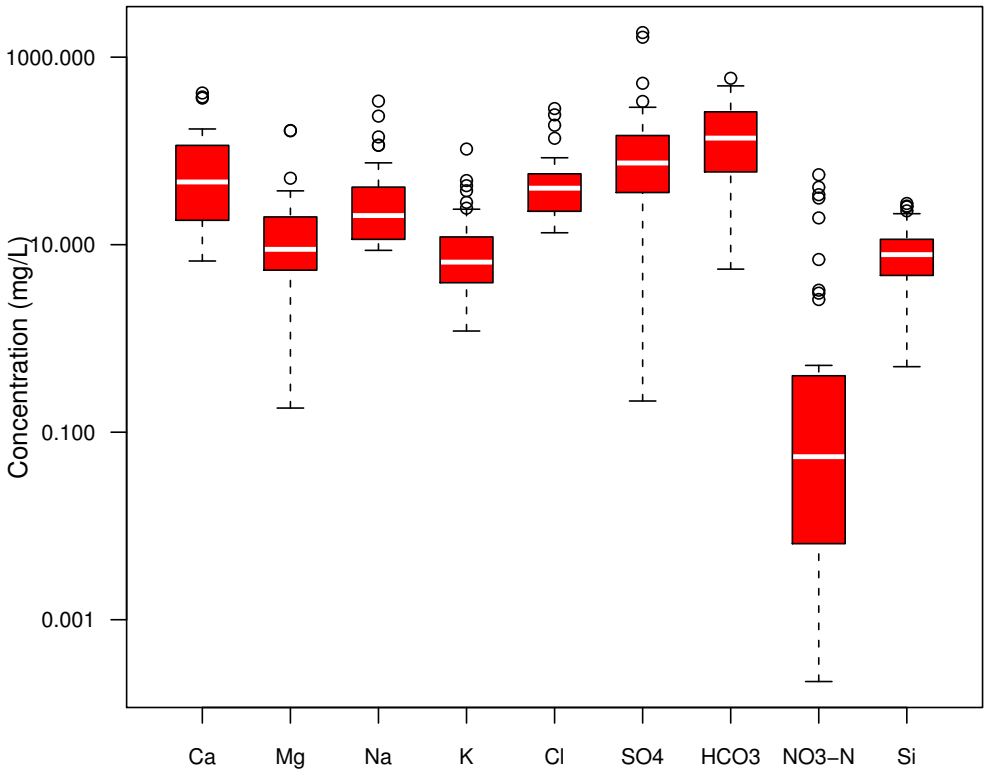

Figure 5.6 Box plots for the major ions in the London Palaeogene aquifer. For an explanation of the box plots see Section 4.3

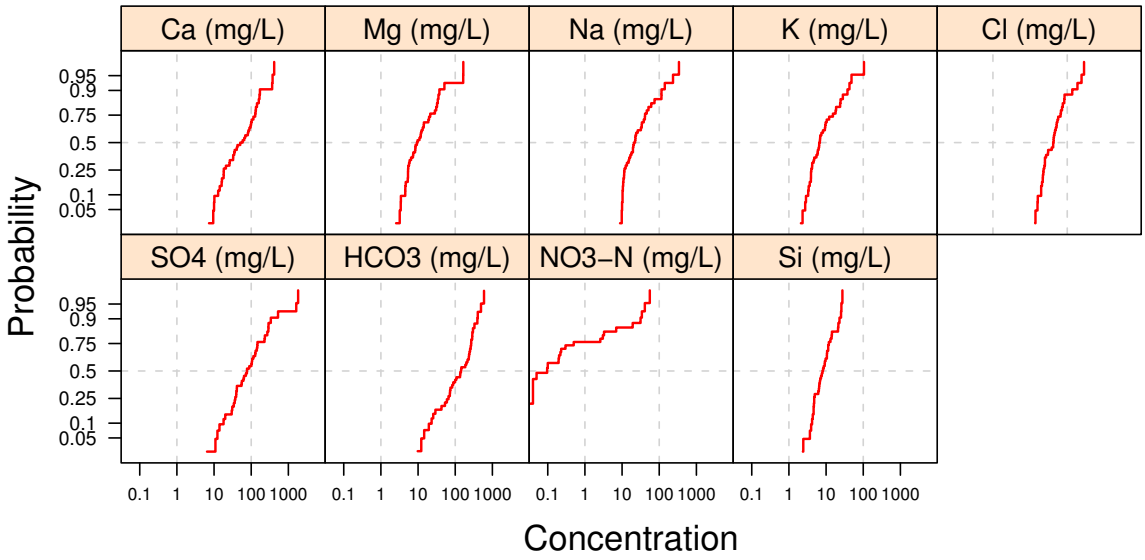

Figure 5.7 Cumulative probability plots for the major ions in the London Palaeogene aquifer

Figure 5.6 and Figure 5.7 indicate the ranges and outliers of the major ions. With the exception of NO_3-N the major ions have similar ranges, having a minimum of <10 mg L^{-1}, a maximum between 100 and 2000 mg L^{-1} and a mean between 20 and 200 mg L^{-1}. In comparison NO_3-N has a minimum below detection and a maximum of 55 mg L^{-1}, this distribution can be attributed to the large variation in redox conditions, e.g. the low NO_3-N concentrations could represent nitrate lost in reducing conditions through denitrification. The shallow curve of the NO_3-N cumulative probability plot implies pollution (after Shand et al., 2007), which is likely in areas where there is agriculture. The remaining major elements have a steep cumulative probability curve, and few outliers, indicating a near log-normal distribution.

Calcium has a range of 6.7 to 415 mg L^{-1}, a 5th to 95th percentile range of 9.5 to 366 mg L^{-1} and a median of 42.6 mg L^{-1}. This is a large range, and is a similar data distribution to that found in the Permo-Triassic sandstones, where the higher Ca concentrations were attributed to gypsum dissolution or mixing with formation water or seawater (Shand et al., 2007). The modelled saturation indices indicate that gypsum and anhydrite are undersaturated in the Palaeogene waters and it is unlikely that these minerals contribute significantly to the Ca concentration. Figure 5.8 shows that the Ca concentrations are higher in the Thames Group and Thanet Formation, while the lower concentrations are found in groundwaters from the Bracklesham Group, and the Lambeth Group. In general the groundwaters taken from the older, deeper units are enriched in Ca, and it is possible that these boreholes touch the underlying Cretaceous Chalk, which would greatly influence the Ca concentration of these groundwaters.

While samples around the Kent coast could be affected by seawater, it seems unlikely that those based around the Lea Valley reservoir chain, the SLARS sites and a site in Normandy [SU 92 51] are affected by this. The spatial concentration distribution of Ca is also mirrored

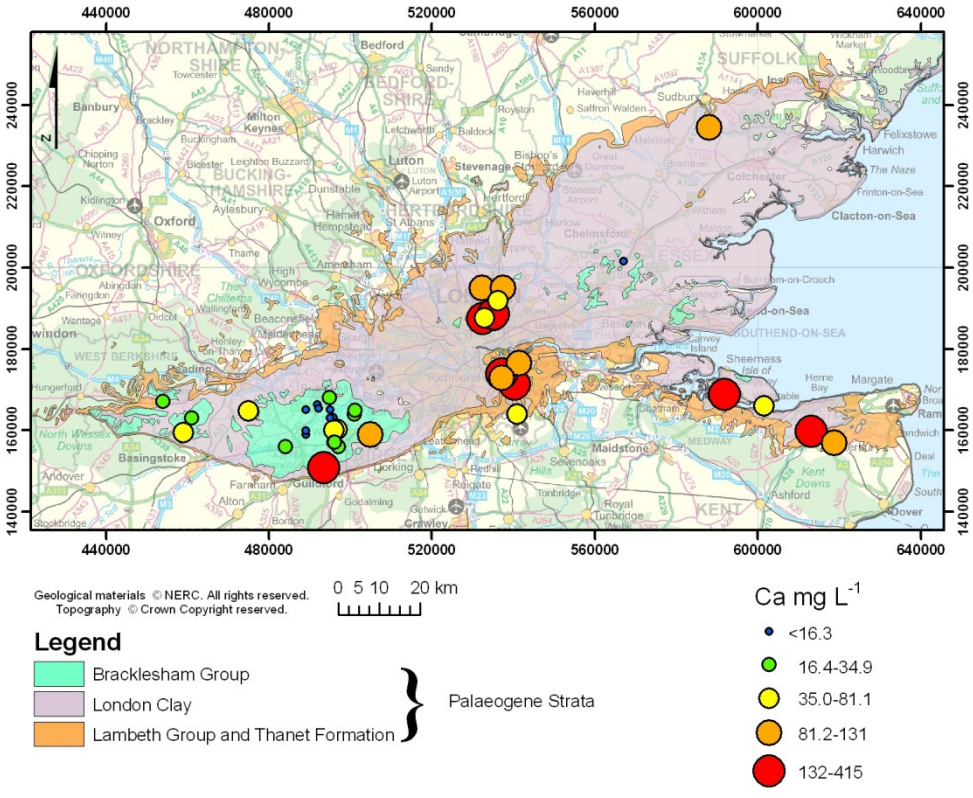

Figure 5.8 Regional variation of Ca within the London Palaeogene aquifer

by the calcite saturation indices. The samples taken from the Bracklesham Formation are predominantly undersaturated, with one sample close to equilibrium. In contrast the samples taken from groundwaters in the Thames Group, Lambeth group, and Thanet Formation are predominantly saturated, reflecting the higher Ca and alkalinity concentrations.

Magnesium has a range of 0.18 to 165 mg L^{-1}, a 5th to 95th percentile range of 3.21 to 51.1 mg L^{-1}, and a median of 8.54 mg L^{-1}. This is a typical concentration range for sandstone aquifers in England, and the main sources are likely to be clay minerals and dolomite (Shand et al., 2007).

Although the concentration range of Mg is smaller than Ca, the spatial distribution is similar. The lowest values are found in the samples taken from the Bracklesham Group aquifer, and the higher values are found in the samples taken from the groundwaters in the Thames Group, Lambeth group, and Thanet Formation (Figure 5.9). This concentration distribution is reflected in the saturation indices for dolomite. The Bracklesham Group samples are all undersaturated with respect to dolomite, reflecting the lack of a source of Mg. Most of the samples from the Thanet Formation are saturated or at equilibrium reflecting the greater availability of Mg. Interestingly the exception to this are the Thanet Formation samples taken in Kent, where the waters are undersaturated with respect to dolomite despite having some of the highest Mg concentrations. These sites lie at the edge of the Thames basin, close to the recharge area; it is possible that these are younger waters, which have not attained saturation because of the low reactivity of dolomite.

Sodium has a range of 8.7 to 340 mg L^{-1}, a 5th to 95th percentile range of 9.8 to 141 mg L^{-1} and a median of 20.1 mg L^{-1}. This is a typical range for sandstone aquifers in England. Rainfall is an important primary source of Na (Shand et al., 2007), although these concentrations greatly exceed the concentrated rainfall value of 4.8 mg L^{-1}. The main minerals

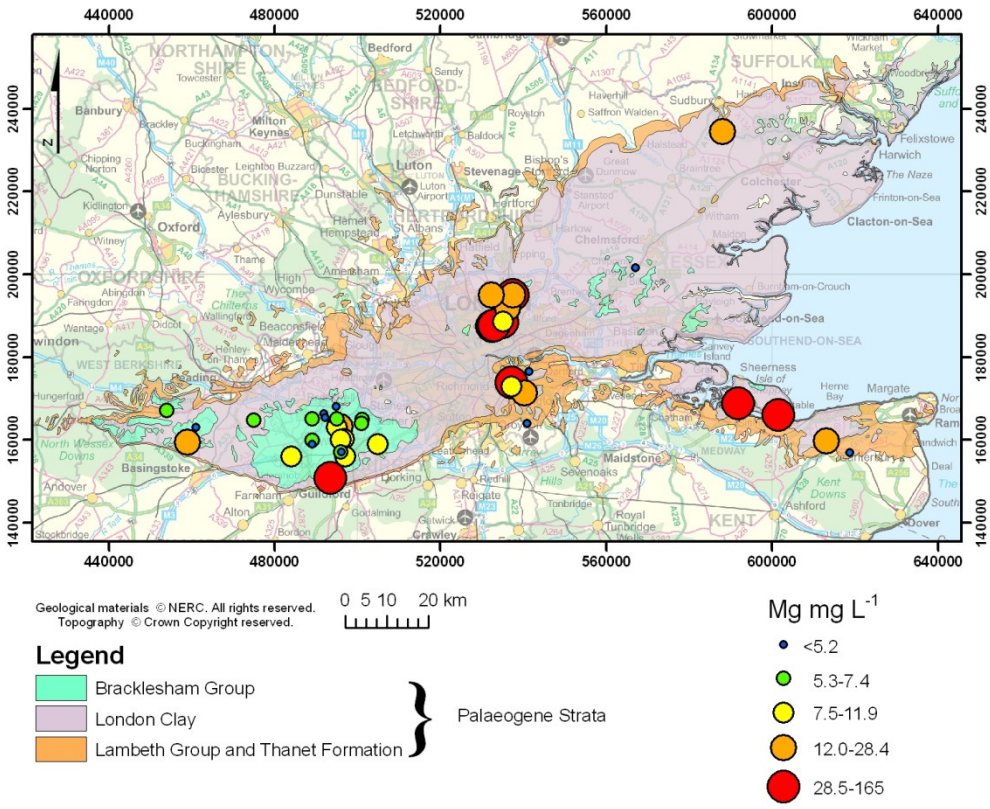

Figure 5.9 Regional variation of Mg within the London Palaeogene aquifer

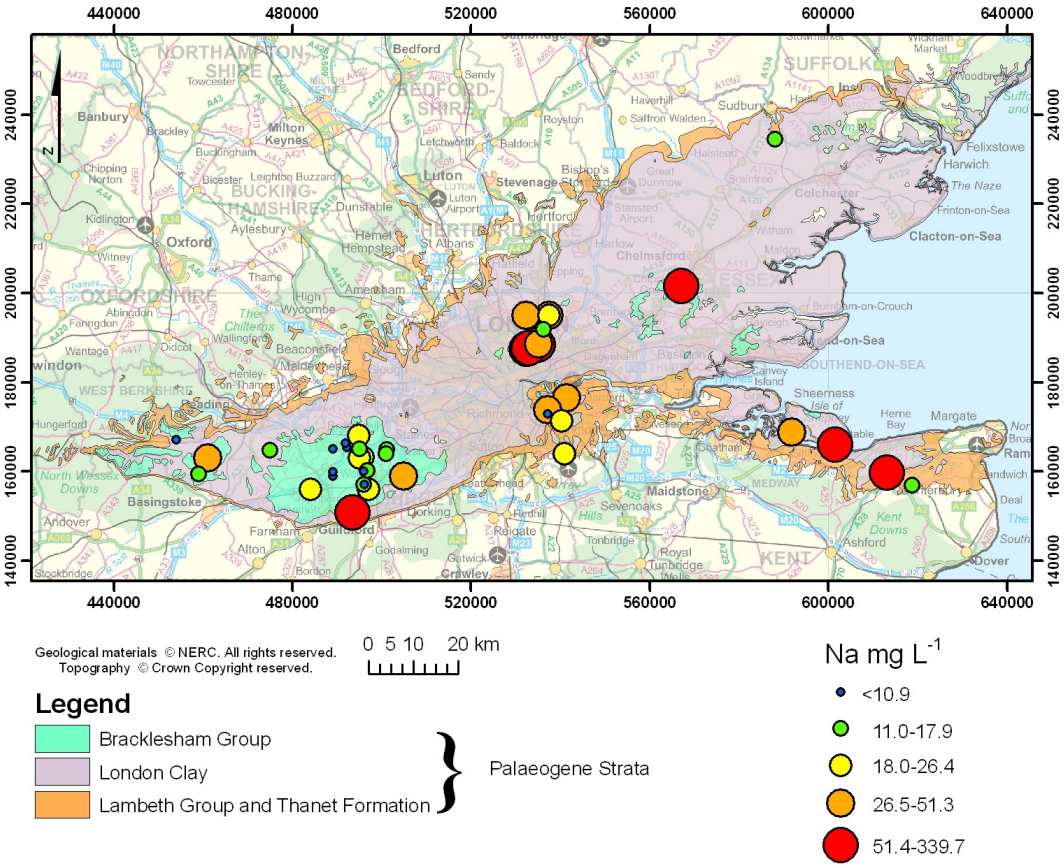

Figure 5.10 Regional variation of Na within the London Palaeogene aquifer

containing Na are clays and plagioclase feldspars and it is likely that these minerals are responsible to some extent for the excesses above concentrated rainfall levels. In the near coastal and estuarine waters, mixing with saline waters will have impacted the concentrations of Na and other solutes. Ion exchange reactions may also be important here, as Na can be sorbed where there is seawater intrusion (Shand et al., 2007).

Figure 5.10 shows the distribution of Na concentrations and demonstrates that it has a similar distribution to the other major ions, in that the lowest concentrations are found in the Bracklesham Group beds, and the higher concentrations are found in and below the London Clay. There is more localised variability within this distribution, indicating localised variations in the bedrock mineralogy or the influence of seawater from the coast, or adjacent to the lower reaches of the Thames.

Potassium has a range of 1.2 to 105 mg L^{-1}, a 5^{th} to 95^{th} percentile range of 2.33 to 42.6 mg L^{1}, and a median of 6.5 mg L^{-1}. This is also fairly typical of English sandstone aquifers. The main baseline sources of K in groundwater are rainfall and dissolution of clays, K-feldspar, and biotite. In addition K can be elevated in groundwaters owing to pollution from fertilisers, but it is unlikely in this environment (Shand et al., 2007). While the general trend is similar to the other major elements discussed above there are localised variations (see Figure 5.11). For instance the groundwaters obtained from boreholes in the Lea Valley have K concentrations that vary from 4.2 to 42 mg L^{-1}, and the K concentrations in the SLARS study groundwaters vary from 2.88-28 mg L^{-1}. The highest concentration is found at the London Clay groundwater site, which probably has a strong influence from clay-mineral dissolution.

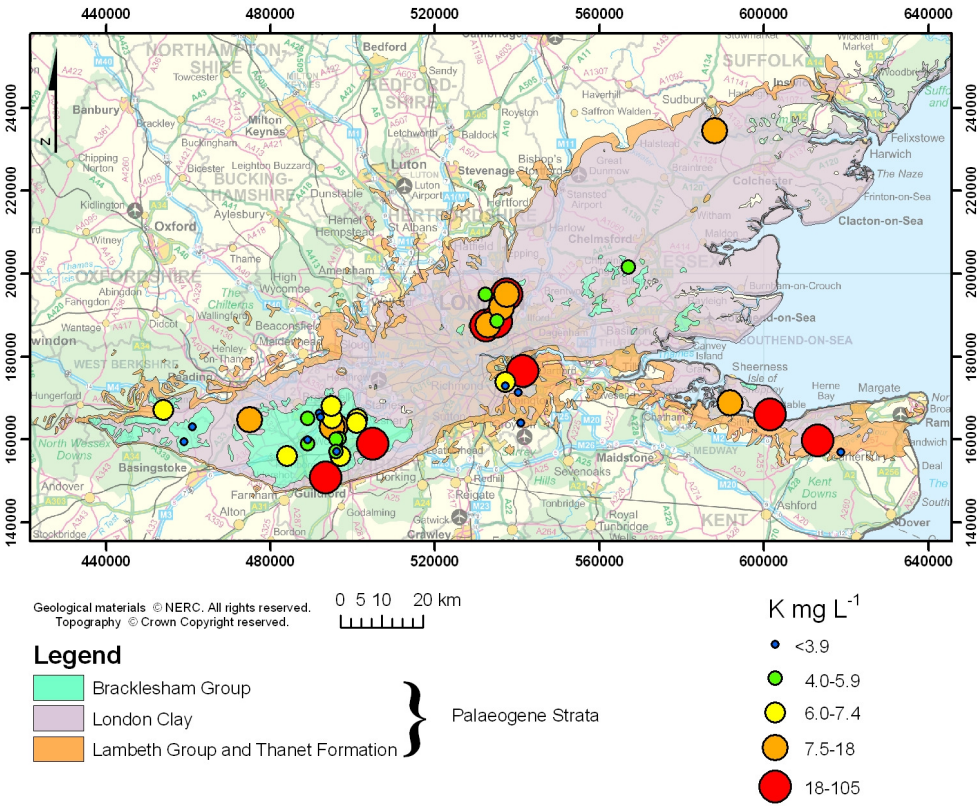

Figure 5.11 Regional variation of K within the London Palaeogene aquifer

Chloride has a range of 13.4 to 283 mg L^{-1}, a 5th to 95th percentile range of 14 to 188 mg L^{-1}, and a median of 38.3 mg L^{-1}. This range is similar to other sandstone aquifers in the UK. The main baseline sources of Cl in groundwater are rainfall or mixing with saline waters (Shand et al., 2007). The spatial distribution (Figure 5.12) is similar to that of Na, suggesting a NaCl source. Like all the major elements the concentrations are generally lower in the Bracklesham Group than in the underlying Thames Group, Lambeth group, and Thanet Formation. A notable exception to this is a site near Pamber Heath which has a Cl concentration in the upper 75th percentile and a Na concentration in the upper 50th percentile. There is no obvious reason for this anomaly, and this site does not show elevated concentrations of other major elements. High concentrations of both Na and Cl close to the coast and the lower reaches of the River Thames may indicate mixing with more saline waters.

Sulphate has a range of 0.22 to 1830 mg L^{-1}, a 5th to 95th percentile range of 10.9 to 527 mg L^{-1}, and a median of 72 mg L^{-1}. This range is larger than that in most English and Welsh major aquifers (after Shand et al., 2007). Indeed the median SO_4 value for 23 major UK aquifers is 28.1 mg L^{-1} (Shand et al., 2007). The main baseline sources of SO_4 in groundwater are rainfall, dissolution of gypsum or oxidation of pyrite (Shand et al., 2007). It is most likely that the higher values represent oxidation of pyrite as this mineral is known to occur sporadically throughout the Palaeogene beds. Some of the high SO_4 concentrations could be attributed to fertiliser use, however, there is no correlation with Cl, P or NO_3-N (all r^2 <0.008), and little correlation with K (r^2=0.3).While the general spatial trend is that the highest concentrations are found in the London Clay and strata below (Figure 5.13), there is a highly variable nature to this spatial distribution, which can be attributed to sporadic occurrences of pyrite.

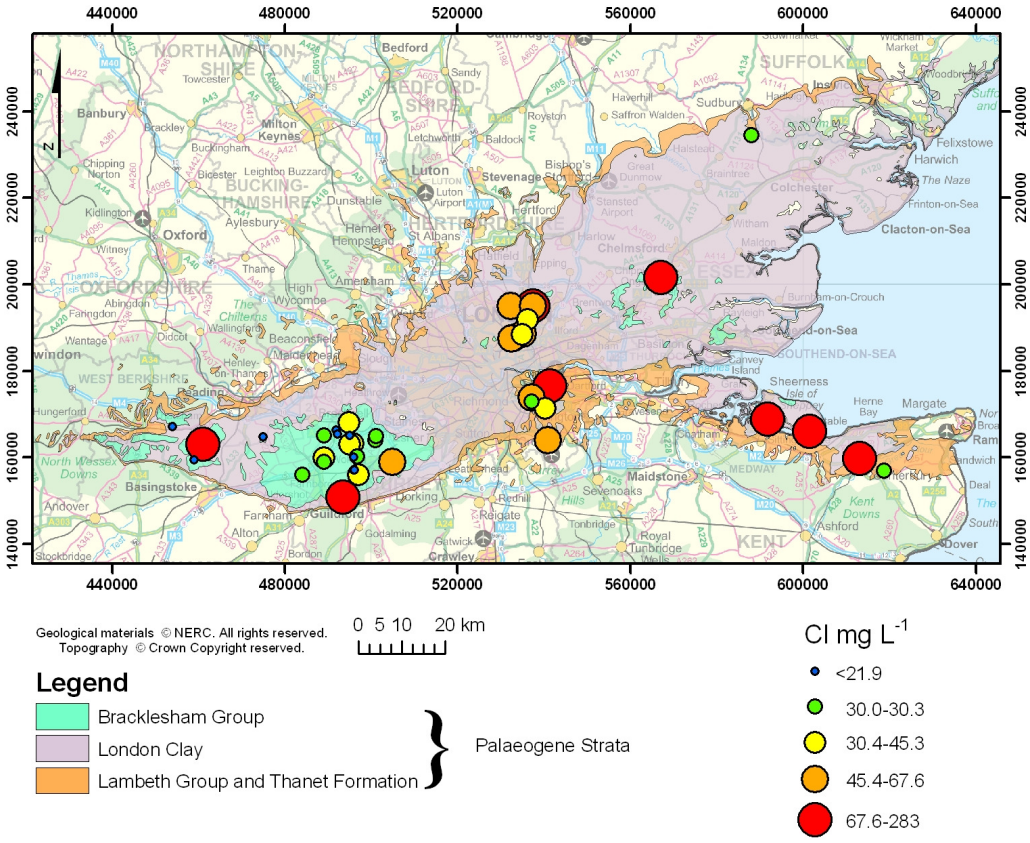

Figure 5.12 Regional variation of Cl within the London Palaeogene aquifer

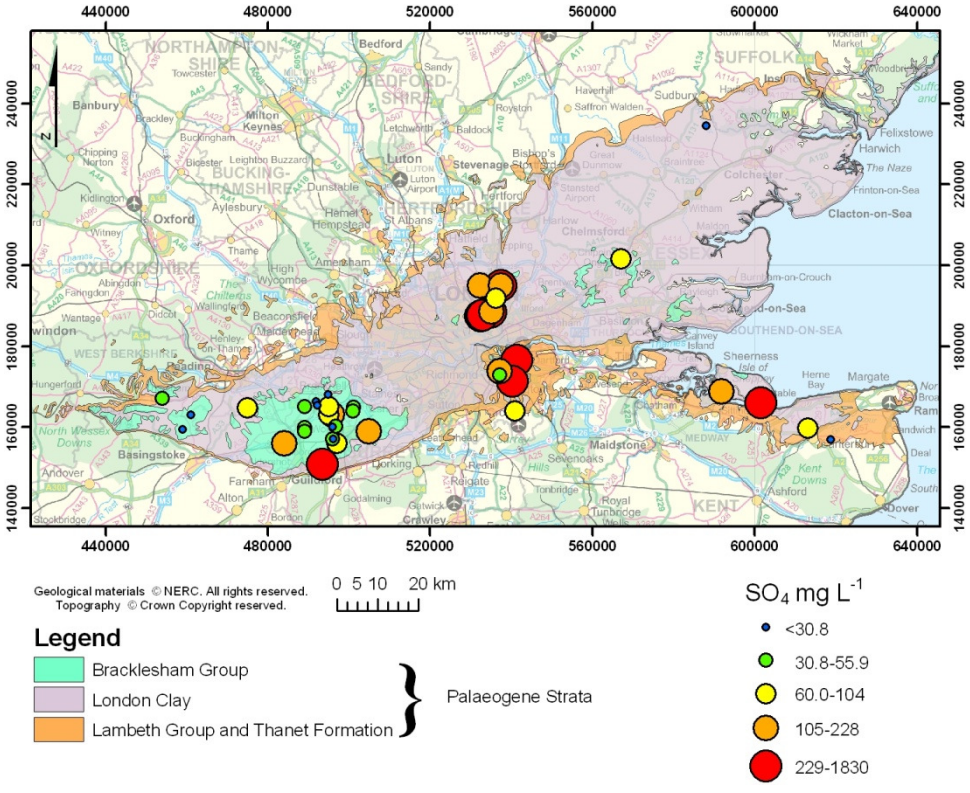

Figure 5.13 Regional variation of SO_4 within the London Palaeogene aquifer

Bicarbonate (alkalinity) has a range of 5.5 to 596 mg L^{-1}, a 5th to 95th percentile range of 12.2 to 404 mg L^{-1}, and a median of 137 mg L^{-1}. The main baseline sources of HCO_3 in groundwater are dissolution of carbonate minerals, silicate hydrolysis, and oxidation of organic matter (Shand et al., 2007).

The spatial distribution (Figure 5.12) of bicarbonate is strongly linked to the geology as the lower concentrations are found in the Bracklesham Group groundwaters, and the highest concentrations are in the London Clay and the units below. The only two exceptions to this are in the SLARS sites. There is a strong correlation with Ca indicating that the alkalinity is probably derived from calcite sources, potentially as a cement between grains. There is a strong relationship between pH and alkalinity and it seems the pH distribution is controlled, at least partially by carbonate mineral dissolution.

Nitrate, as N, has a range of <0.02 to 55.7 mg L^{-1}, a 5th to 95th percentile range of <0.02 to 34 mg L^{-1}, and a median of 0.055 mg L^{-1}. This negatively skewed distribution is commonly found in confined sandstone aquifers in the UK (after Shand et al., 2007). Values below the concentrated rainfall value of 1.56 mg L^{-1} can be attributed to baseline alone. However values above this are most likely caused by diffuse agricultural pollution which affects the majority of UK aquifers (Shand et al., 2007). The distribution of NO_3-N hence does not follow the other major elements as it is probably distributed according to diffuse inputs (Figure 5.15). Five of the sites exceed the national drinking-water limit (11.3 mg L^{-1}), and would require treatment if they were to be used for this purpose (OPSI, 2000).

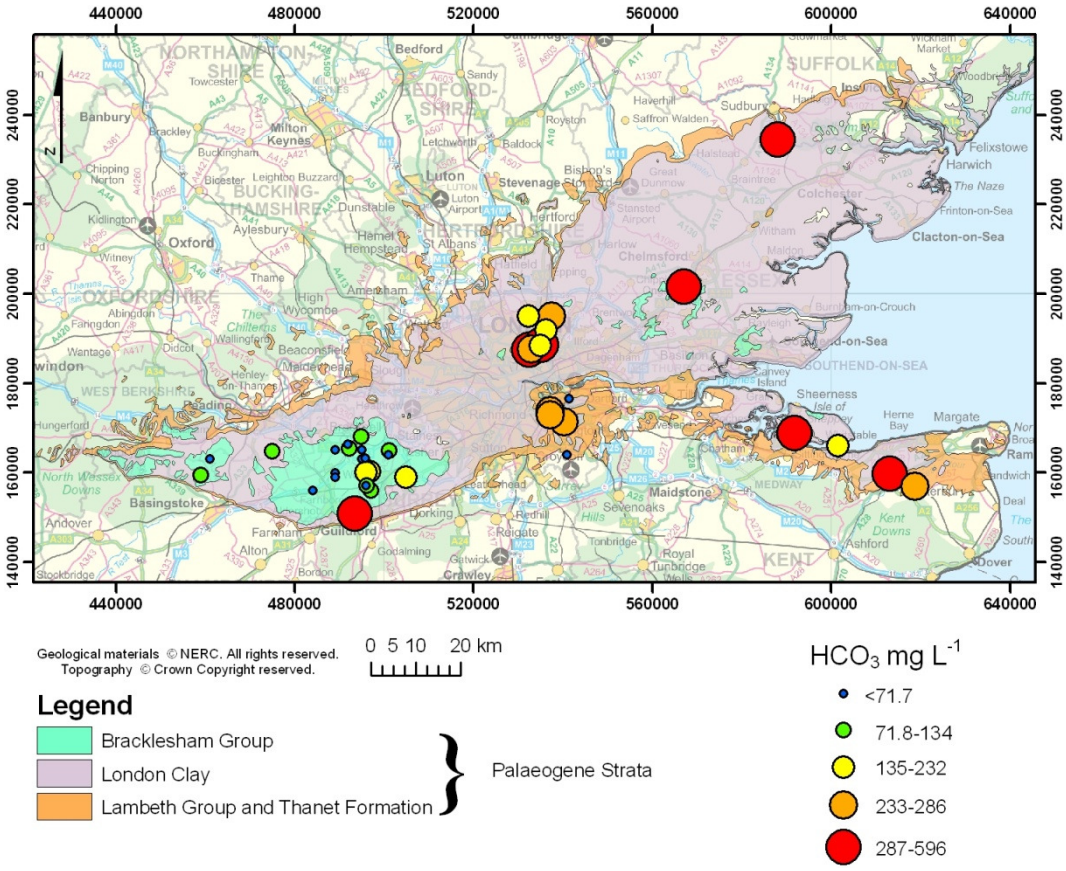

Figure 5.14 Regional variation of HCO_3 within the London Palaeogene aquifer

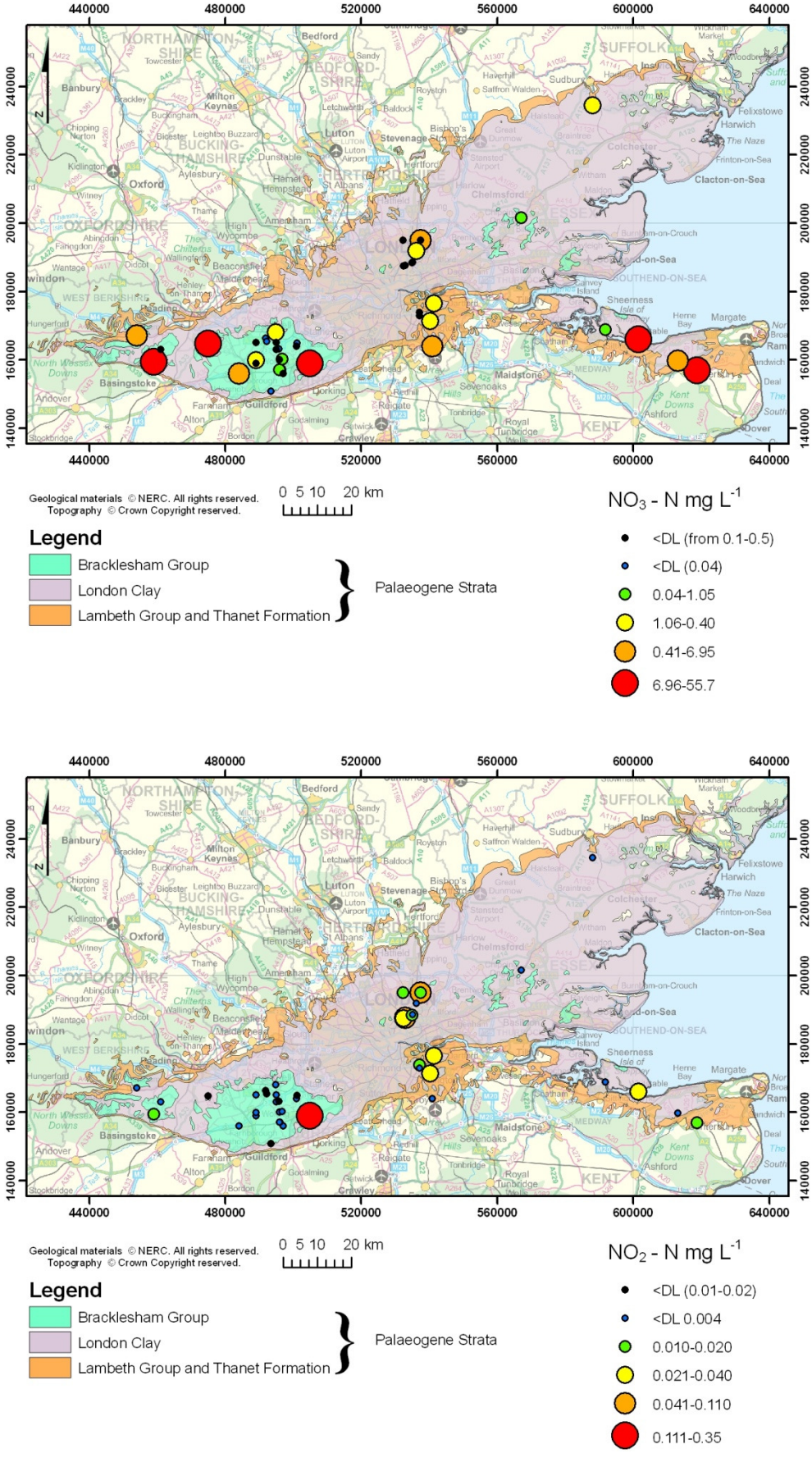

Figure 5.15 Regional variation of NO_3-N (top) and NO_2-N (bottom) within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

Nitrite, as N, has a range of <6 × 10^{-4} to 0.35 mg L^{-1}, a 5th to 95th percentile range of 2 × 10^{-4} to 0.05 mg L^{-1}, and a median of 0.002 mg L^{-1}. It is produced as an intermediate metastable N species, its presence can indicate the process of denitrification under strongly reducing conditions. Unlike NO_3-N, NO_2-N appears to follow the geological trends seen for most major elements. There is a cluster of sites where the groundwater contains no detectable NO_2-N in the Bracklesham Group, and the highest concentrations are found in the units below the London Clay. This does not correlate very well with Eh or DO. Nitrite can be an indicator of pollution from agriculture or domestic waste, and, aside from the highest value many of the measurable NO_2-N concentrations appear to be in groundwaters under urbanised areas. It is very difficult to distinguish these anthropogenic inputs and determine the likely range of baseline NO_2-N concentrations.

Ammonium, as N, has a range of <0.1 to 6.7 mg L^{-1}, a 5th to 95th percentile range of 0.006 to 0.94 mg L^{-1}, and a median of 0.069 mg L^{-1}. It is found as the NH_4 ion, which is strongly sorbed onto mineral surfaces, and is stable under reducing conditions. While high NH_4 can be associated with pollution, it is not unusual to find concentrations of 1 mg L^{-1}, and up to 10 mg L^{-1} in old reducing groundwaters (Shand et al., 2007). There is a sporadic spatial

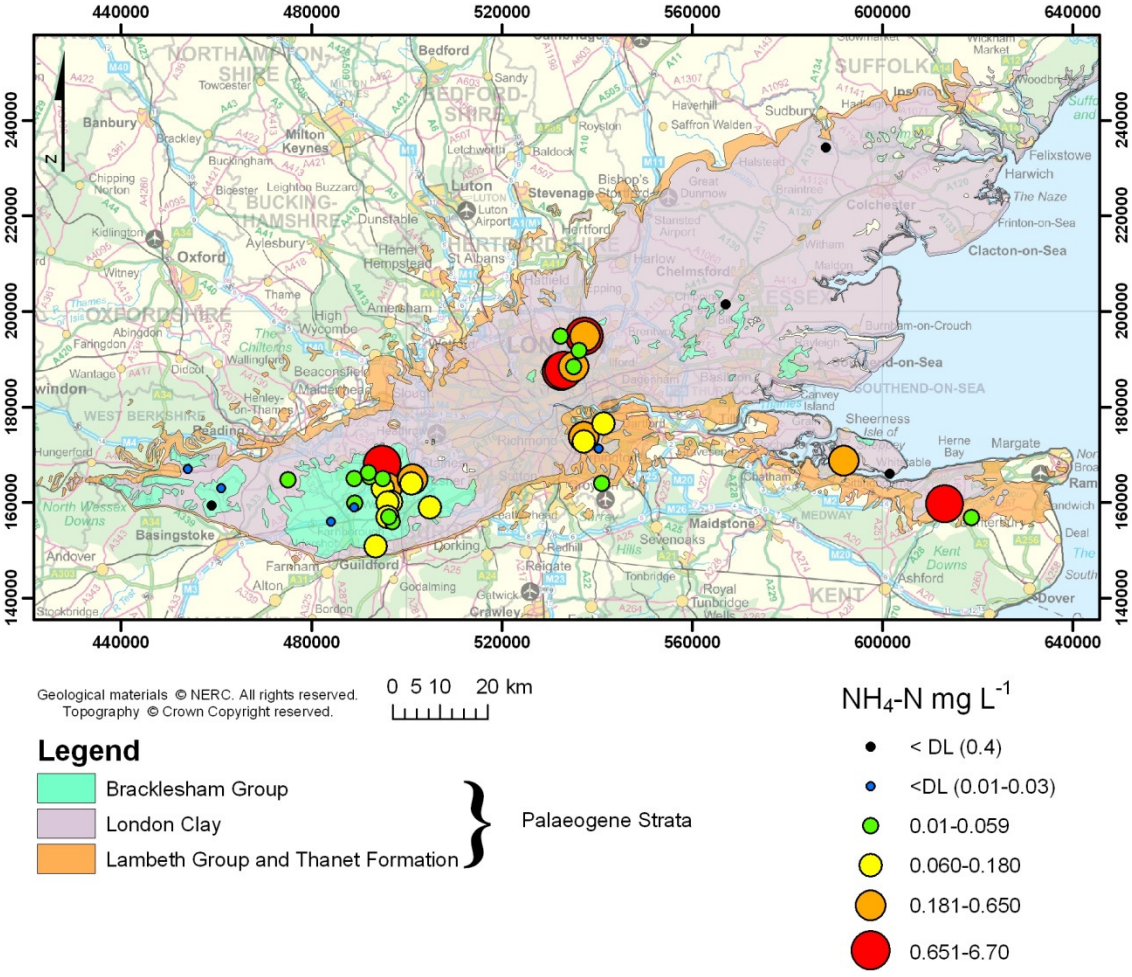

Figure 5.16 Regional variation of NH_4-N within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

distribution (Figure 5.16) which reflects the wide range of Eh conditions. The groundwater sample with the highest concentration is strongly reducing, indicating that nitrate reduction has occurred. It seems there are "pockets" of reduced groundwaters throughout the London Palaeogene beds. There is a weak negative correlation between the Eh and the NH_4-N concentration, suggesting that nitrate reduction occurs under the most reducing conditions. However, several fully oxidised sites have a relatively high NH_4-N concentration. Most notable is a site along the Kent coast, where the groundwater has not been pumped for a few years and has a NH_4-N concentration of 0.94 mg L^{-1}. This could indicate there is pollution from slurry, sewage or fertiliser.

Dissolved organic carbon (DOC) has a range of 0.35 to 45.3 mg L^{-1}, a 5th to 95th percentile range of 0.37 to 12.4 mg L^{-1}, and a median of 1.34 mg L^{-1}. The range spans over an order of magnitude, which is typical of DOC in UK groundwaters (Shand et al., 2007). In this study DOC represents the sum of organic material (mainly macro molecules of humic and fulvic acids) which pass through an Ag-membrane filter with a pore size of 0.45 µm. Dissolved organic carbon is mostly derived from soil reactions, but it can also be enhanced by pollution inputs, such as slurry pits, fertilisers, or landfills (Shand et al., 2007). There are limited DOC analyses and there appears to be no spatial trend.

Silicon has a range of 0.5 to 27.5 mg L^{-1}, a 5th to 95th percentile range of 2.44 to 25.3 mg L^{-1} and a median of 7.67 mg L^{-1}. This is a fairly typical range for Si in UK aquifers (Shand et al., 2007), and the limited range represents a rapid attainment of SiO_2 saturation. Despite the abundance of Si in the Earth's crust (it is the second most abundant element); the concentrations of Si are relatively low, owing to a low solubility (Hem, 1992). The

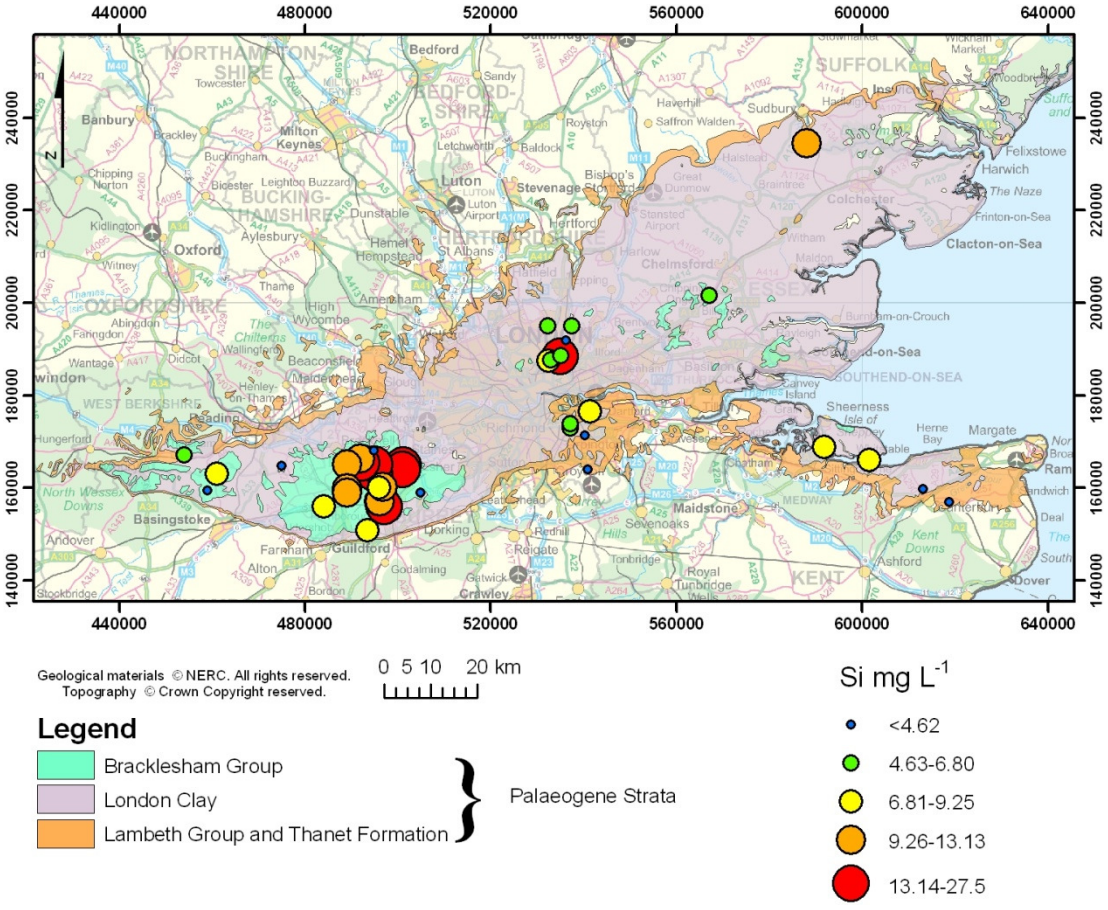

Figure 5.17 Regional variation of Si within the London Palaeogene aquifer

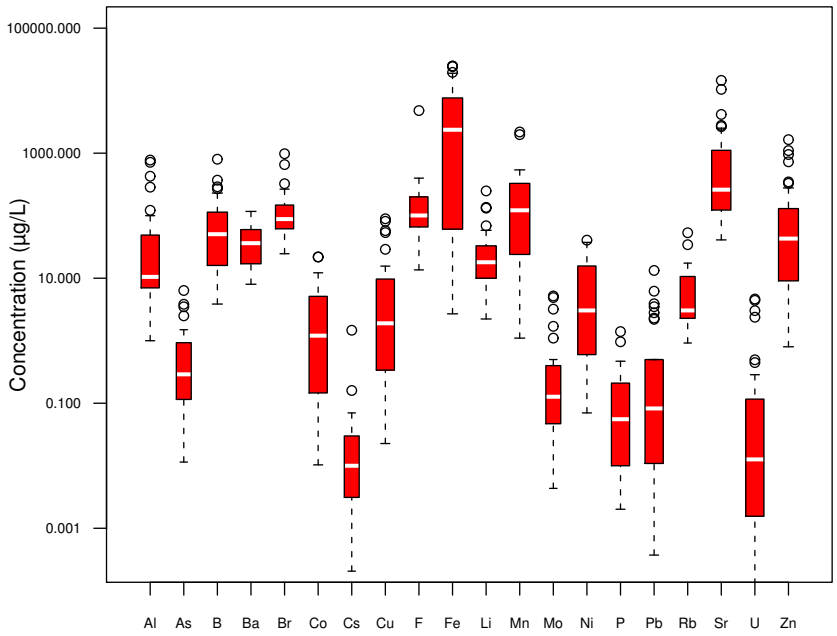

Figure 5.18 Box plots for the minor and trace elements in the London Palaeogene aquifer. For an explanation of the box plots see Section 4.3

concentrations of Si are related to the solubility of SiO_2, which has a series or polymorphs; of these amorphous SiO_2 is the most soluble and quartz is the least soluble (Hem, 1992). In the modelled saturation indices, quartz was mostly close to saturation in the groundwaters, whereas amorphous SiO_2 is universally undersaturated. The Si is generally more concentrated in the younger Bracklesham Group beds, than in the Thames Group, Lambeth Group, or Thanet Formation (see Figure 5.17). This general trend could be caused by increased SiO_2 solubility in the waters with lower pH values.

5.2 MINOR AND TRACE CONSITUENTS

Summary statistical data for minor and trace constituents are presented in Figure 5.18.and Figure 5.19. In addition spatial variations are presented in Figure 5.20 to Figure 5.41. Where all the determinations of an element are below detection the element is not discussed here. There is a wide range of concentrations, and of particular note is Fe, which spans almost five orders of magnitude.

5.2.1 Phosphorus

Phosphorus has a range of <0.01 to 1.4 mg L^{-1}, and a median of 0.041 mg L^{-1}. A 5th percentile was not produced in the summary statistics owing to the large number of non-detects, the 95th percentile is 0.96 mg L^{-1}. This is typical concentration range of P measured in the major aquifers described in Shand et al. (2007). The cumulative frequency plot (Figure 5.19) indicates the P analyses represent one population. Dissolved P in groundwaters can be derived from a variety of natural as well as anthropogenic sources. Potential mineral sources include phosphate minerals, organic matter, and exchangeable P from Fe oxides. Anthropogenic sources include fertilisers, effluent from water treatment and slurry (Shand et al., 2007).

The spatial distribution shows there is a cluster of the highest values in the east of the Bracklesham Group outcrop (Figure 5.20). Most of the remaining sample sites have low concentrations of P. This distribution does not correlate with other indicators of agricultural

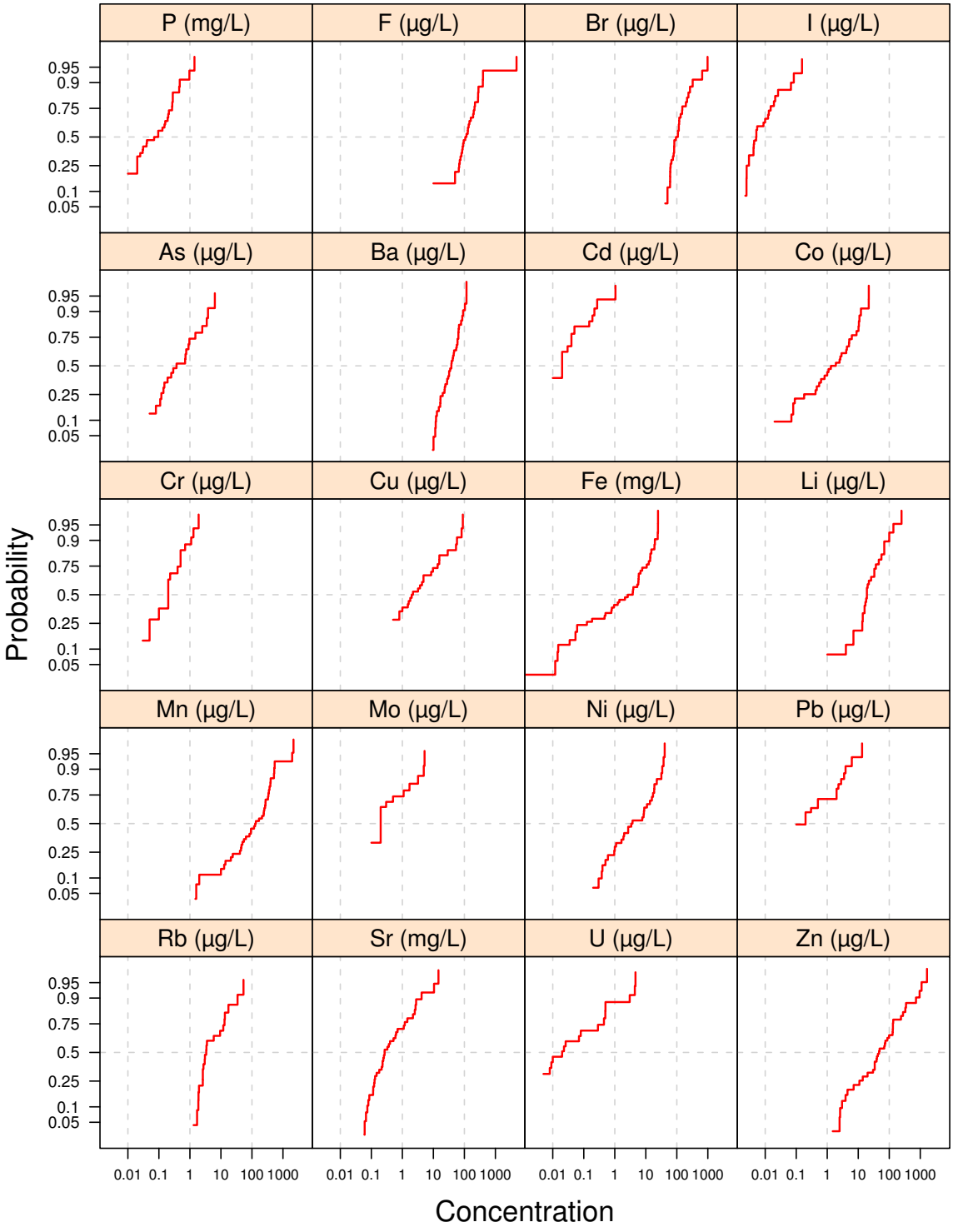

Figure 5.19 Cumulative probability for selected trace elements in the groundwater from the London Palaeogene aquifer.

Table 5.2 Statistical summary of data for minor and trace elements.

	units	n	n(c)	min	mean	max	P0	P5	P25	P50	P75	P90	P95
Ag	µg/L	20	20	<0.005		<0.005							
Al	µg/L	34	2	<10	84	776		1	7	10	49	286	714
As	µg/L	23	3	<0.05	1.03	6.36			0.11	0.29	0.96	3.49	3.83
B	µg/L	42	14	<10	100	801			15	57	114	230	290
Ba	µg/L	42	0	8	42.6	117		10.1	17	34.7	60	85.6	104
Be	µg/L	34	18	<0.005	0.0992	1.1	0.0011	0.002	0.00969	0.0198	0.0394	0.11	0.645
Br	mg/L	34	2	<0.05	0.151	0.98		0.0328	0.0616	0.083	0.148	0.266	0.657
Cd	µg/L	34	19	<0.01	0.0661	1.05	9.46E-05	0.000239	0.00168	0.01	0.0291	0.178	0.237
Ce	µg/L	23	2	<0.01	2.71	46			0.01	0.05	0.12	4.73	10.6
Co	µg/L	34	4	<0.02	4.06	21.9			0.09	1.1	5.13	10.9	21.8
Cr	µg/L	34	18	<0.03	0.25	1.91	0.00449	0.00883	0.0286	0.1	0.225	0.64	1.17
Cs	µg/L	23	7	<0.01	0.0904	1.47				0.01	0.03	0.07	0.16
Cu	µg/L	34	9	<0.5	12	89.2		0.06	0.06	1.8	9.7	53.7	81.3
Dy	µg/L	23	8	<0.005	0.237	4.16				0.007	0.023	0.231	0.632
Er	µg/L	23	11	<0.005	0.124	2				0.006	0.023	0.147	0.396
Eu	µg/L	23	11	<0.005	0.0759	1.15				0.006	0.015	0.146	0.234
F	mg/L	34	6	<0.01	0.269	4.8			0.066	0.095	0.2	0.284	0.399
Fe	µg/L	42	2	<0.5	5820	24800		6	61	2130	7660	19000	24200
Ga	µg/L	23	21	<0.05		0.23							
Gd	µg/L	23	5	<0.005	0.342	5.9			0.006	0.01	0.024	0.425	1.05
Hf	µg/L	23	23	<0.02		<0.02							
Ho	µg/L	23	14	<0.005	0.0464	0.8	3.75E-06	1.50E-05	0.00015	0.00092	0.006	0.0466	0.127
La	µg/L	23	3	<0.01	1.24	19.7		0.007	0.008	0.023	0.068	2.83	4.45
Li	µg/L	42	14	<1	32	249			10	18	33	69	132
Lu	µg/L	23	18	<0.005	0.0131	0.174	6.09E-06	2.01E-05	0.000146	0.000607	0.00388	0.025	0.0513
Mn	µg/L	42	2	<2	259	2180		1.5	24	117	329	512	541
Mo	µg/L	23	13	<0.2	0.799	5.2	0.00435	0.00985	0.047	0.127	0.4	2.9	4.73
Nb	µg/L	23	23	<0.01		<0.01							
Nd	µg/L	23	3	<0.01	1.37	21.2		0.006	0.011	0.032	0.082	2.41	5.94
Ni	µg/L	34	2	<0.2	9.36	40.6		0.07	0.6	2.7	15.7	31.7	37.4
P	mg/L	34	9	<0.01	0.175	1.4			0.01	0.041	0.21	0.45	0.961
Pb	µg/L	34	19	<0.1	1.09	13.3	0.000372	0.00164	0.0119	0.0825	0.45	3.29	4.7
Pr	µg/L	23	8	<0.005	0.299	4.69				0.008	0.018	0.4	1.26
Rb	µg/L	23	0	0.92	8.49	53.4		1.31	1.96	3.05	11.9	17.4	34.4
Sb	µg/L	34	16	<0.005	0.149	1.27			0.005	0.01	0.165	0.518	0.983
Se	µg/L	23	2	<0.01	0.474	4.5		0.01	0.01	0.03	0.54	1	1.3
Sm	µg/L	23	7	<0.005	0.281	4.29			0.005	0.009	0.021	0.69	1.04
Sn	µg/L	34	15	<0.1	0.25	1.5			0.1	0.1	0.3	0.6	0.7
Sr	µg/L	38	0	41	1310	14600		60	123	254	1110	2780	10500
Ta	µg/L	23	23	<0.02		<0.02							
Tb	µg/L	23	18	<0.005	0.0429	0.769	7.63E-08	5.09E-07	1.10E-05	0.000144	0.00171	0.0418	0.115
Th	µg/L	34	33	<0.05		0.08							
Ti	µg/L	34	13	<0.1	1.52	6.6			0.7	1.4	2	2.6	3.1
Tl	µg/L	23	21	<0.01		0.1							
Tm	µg/L	23	18	<0.005	0.0145	0.23	1.07E-06	4.39E-06	4.50E-05	0.00031	0.0020	0.021	0.048
U	µg/L	34	18	<0.005	0.484	4.65	4.48E-05	0.000133	0.00166	0.0126	0.107	1.81	3.52
V	µg/L	34	23	<0.1	0.734	12.3	0.00138	0.00298	0.019	0.0743	0.3	0.959	3.09
W	µg/L	23	20	<0.02		0.15							
Y	µg/L	23	0	0.01	1.37	22.6		0.01	0.032	0.055	0.147	1.71	4.65
Yb	µg/L	23	11	<0.005	0.0875	1.22				0.007	0.023	0.155	0.317
Zn	µg/L	41	3	<20	173	1650		1.5	7.1	43	130	347	952
Zr	µg/L	23	18	<0.02	0.9								

P= percentile; n(c) = number censored; min and max are observed values

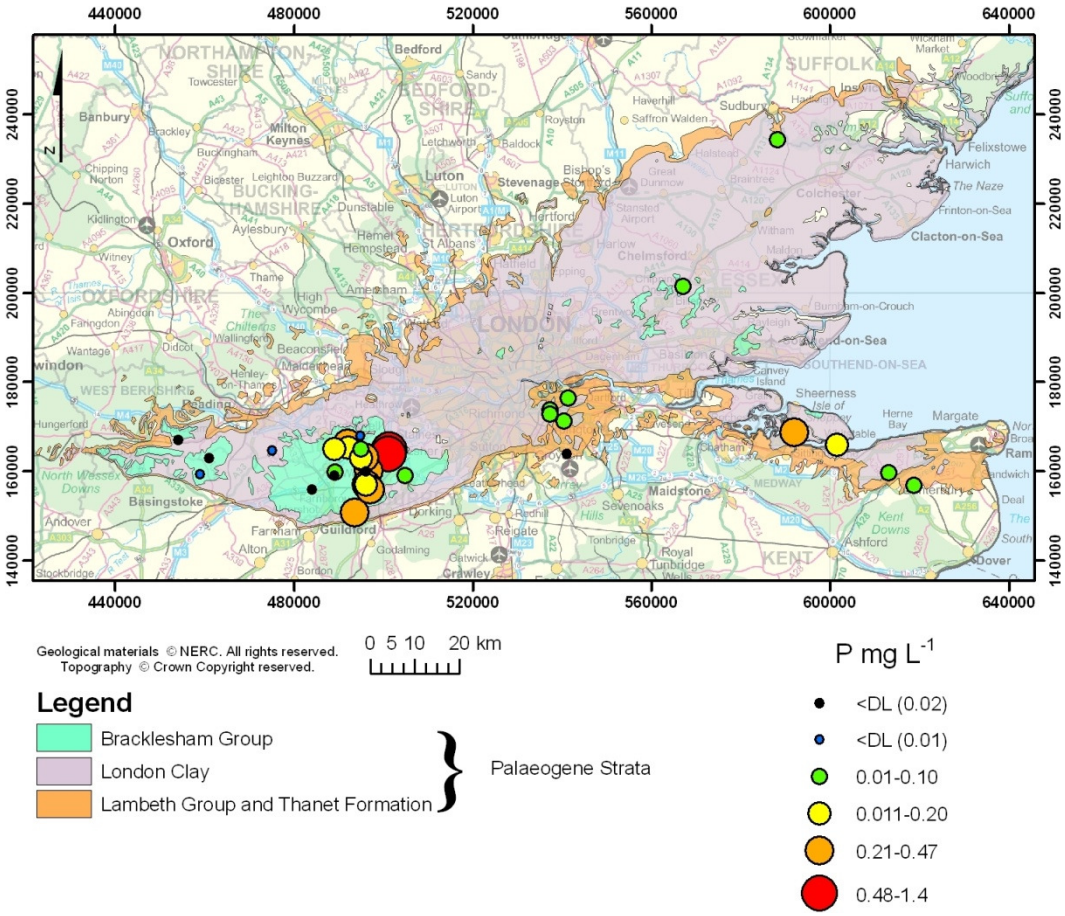

Figure 5.20 Regional variation of P within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

pollution such as K, NO_3-N, and DOC. Where P values were above the 75th percentile the NO_3-N was mostly below the detection limit, with only 2 measurable analyses. Where P values were above the 75th percentile DOC and K values were all below the 75th percentile, except one site near Normandy (the London Clay site), which had the maximum K and DOC values. The sample was taken from a disused well in the back garden of a farm house. It is likely that agricultural pollution has affected this site, and it is possibly the reason the groundwater is no longer used.

5.2.2 Halogen elements

Fluoride has a range of <0.01 to 4.8 mg L^{-1}, and a median of 0.095 mg L^{-1}. The 5th to 95th percentile range is <0.01 to 0.399 mg L^{-1}. The maximum value is an outlier, which exceeds the drinking water limit of 1.5 mg L^{-1} (OPSI, 2000), and other than this the samples range up to 0.399 mg L^{-1}. This range is relatively small, although it is not unusual when compared to other sandstone aquifers in England (Shand et al., 2007).

Fluoride concentrations in rainfall are generally low, so the predominant input tends to be from water-rock interactions (Shand et al., 2005). Where F is below detection the saturation index of fluorite cannot be modelled. However where F was detectable the solutions were all undersaturated with respect to fluorite. This reflects the low F concentrations in the London Palaeogene aquifer. The concentrations of F are lowest in samples taken from the east of the Bracklesham Group outcrop (Figure 5.21).

Bromide has a range of <0.05 to 0.98 mg L^{-1}, a 5th to 95th percentile range of 0.033 to 0.0.66 mg L^{-1}, and a median of 0.062 mg L^{-1}. The Br distribution is similar to that of the major elements (Figure 5.22). Most of the lower concentrations are located in the

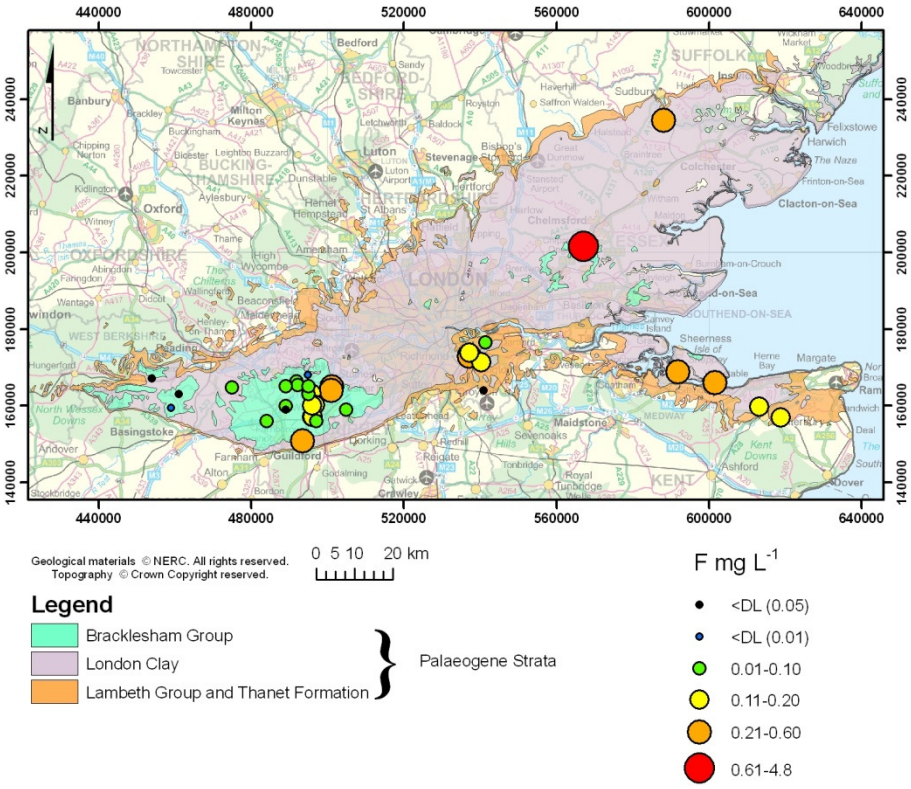

Figure 5.21 Regional variation of F within the London Palaeogene aquifer Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

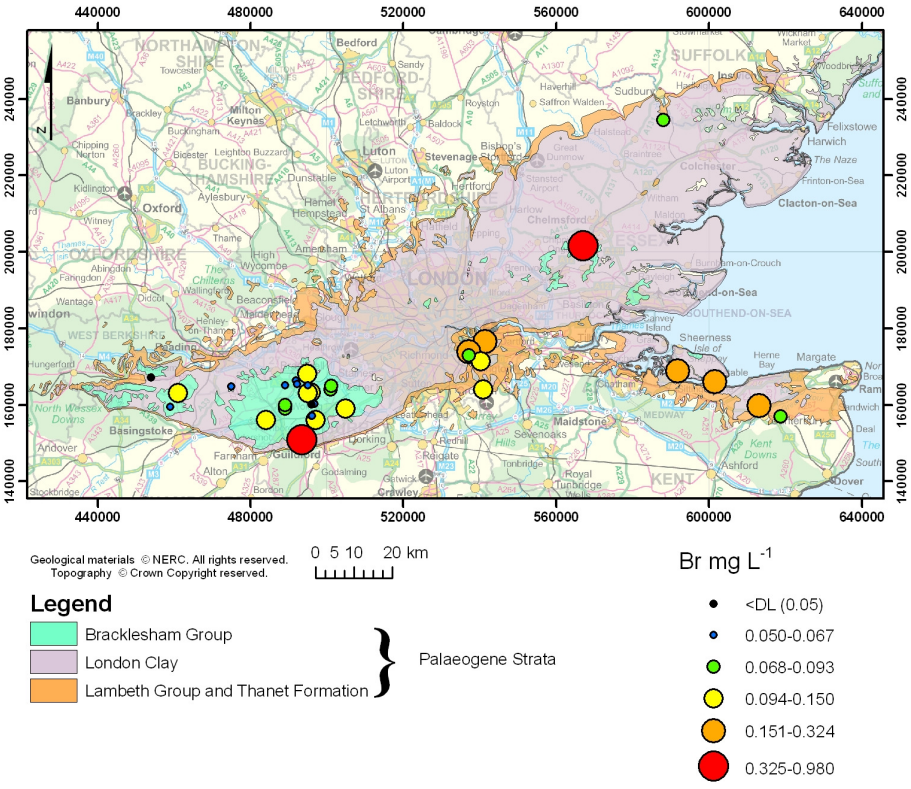

Figure 5.22 Regional variation of Br within the London Palaeogene aquifer

Bracklesham Group beds, whereas the higher concentrations are found below the London Clay. The geochemistry of Br is very similar to that of Cl and thus the two elements are usually well correlated, and the data collected in this study show a good correlation ($r^2 = 0.6$). The Br/Cl ratio is a good indicator of small changes in Br concentrations, and can be a useful indicator of the source of salinity; deviations from the seawater ratio (3.47×10^{-3}) are indicative of non marine sources and geochemical processes. The samples are mostly depleted, and there is no clear spatial distribution of the magnitude of the ratio. Depleted Br/Cl ratios are commonly indicative of halite dissolution, however the variable nature displayed by these groundwaters is likely to be due to variable anthropogenic inputs, thus it is difficult to draw conclusions from these data (Edmunds, 1996).

Iodine occurs in most aqueous environments as the negatively charged iodide. Iodide has a range of <0.003 to 0.154 mg L^{-1}, a 5th to 95th percentile range of 0.0019 to 0.084 mg L^{-1}, and a median of 0.0044 mg L^{-1}. This range is typical of sandstone aquifers in England. Like Cl and Br it generally displays conservative behaviour. Iodine is commonly associated with organic matter, indeed I is generally measurable where the DOC is highest and these two constituents correlate well ($r^2 = 0.7$). The lowest concentrations are generally found in the Bracklesham Group beds, the higher concentrations are found in the London Clay and the beds beneath this (see Figure 5.23 and Figure 2.5).

5.2.3 Alkaline earth elements

Barium has a range of 8 to 117 µg L^{-1}, a 5th to 95th percentile range of 10.1 to 104 µg L^{-1}, and a median of 34.7 µg L^{-1}. These concentrations are relatively low for sandy aquifers in England

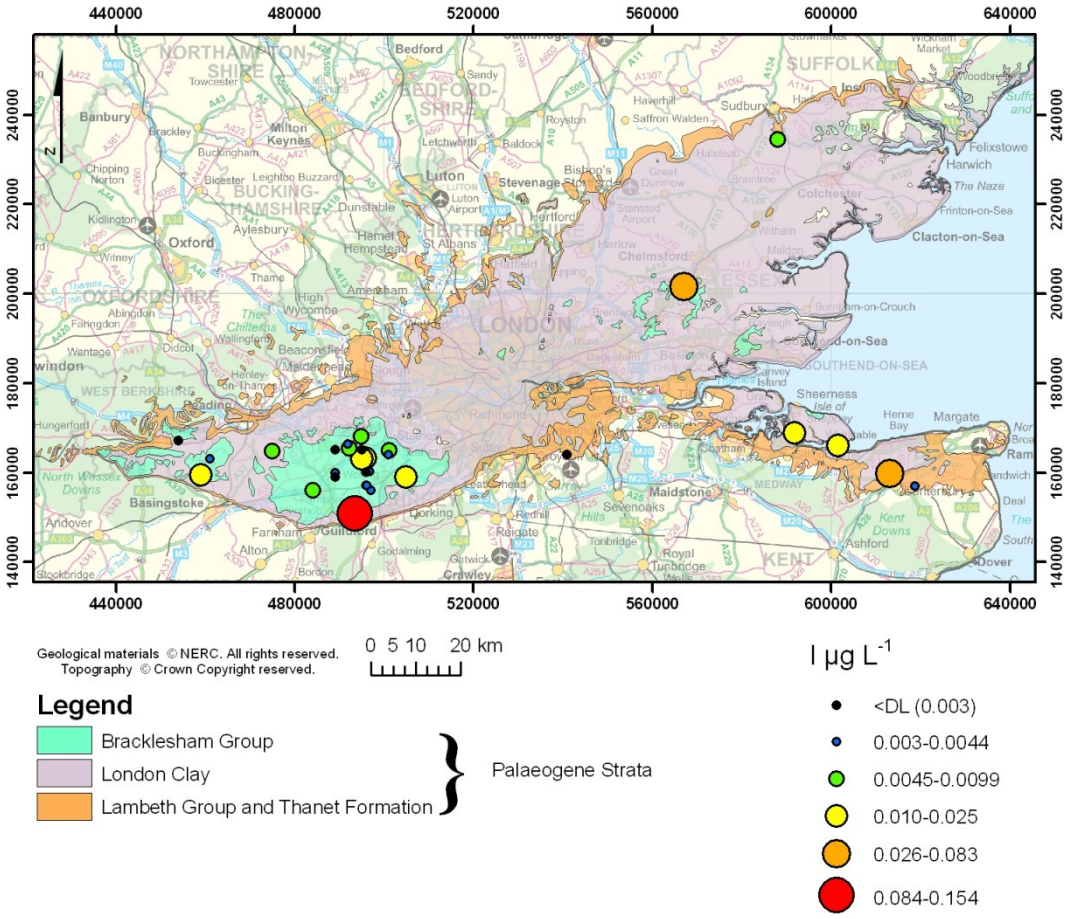

Figure 5.23 Regional variation of I within the London Palaeogene aquifer

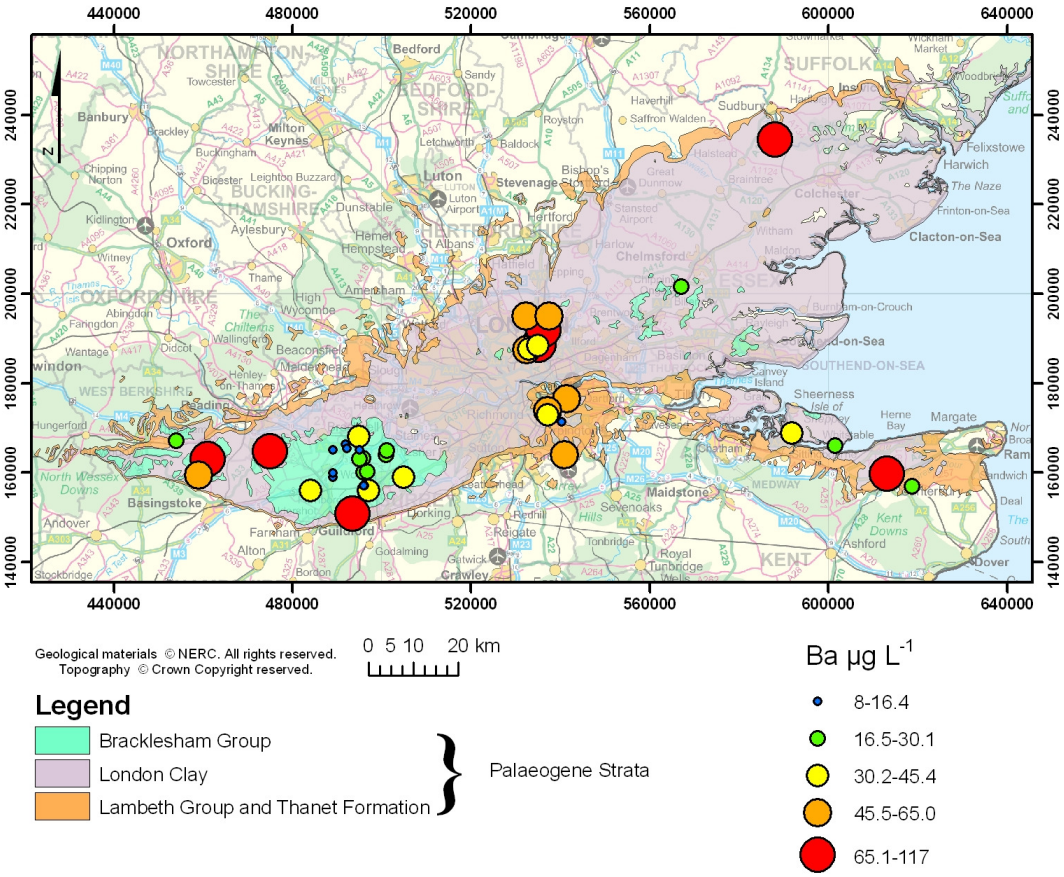

Figure 5.24 Regional variation of Ba within the London Palaeogene aquifer

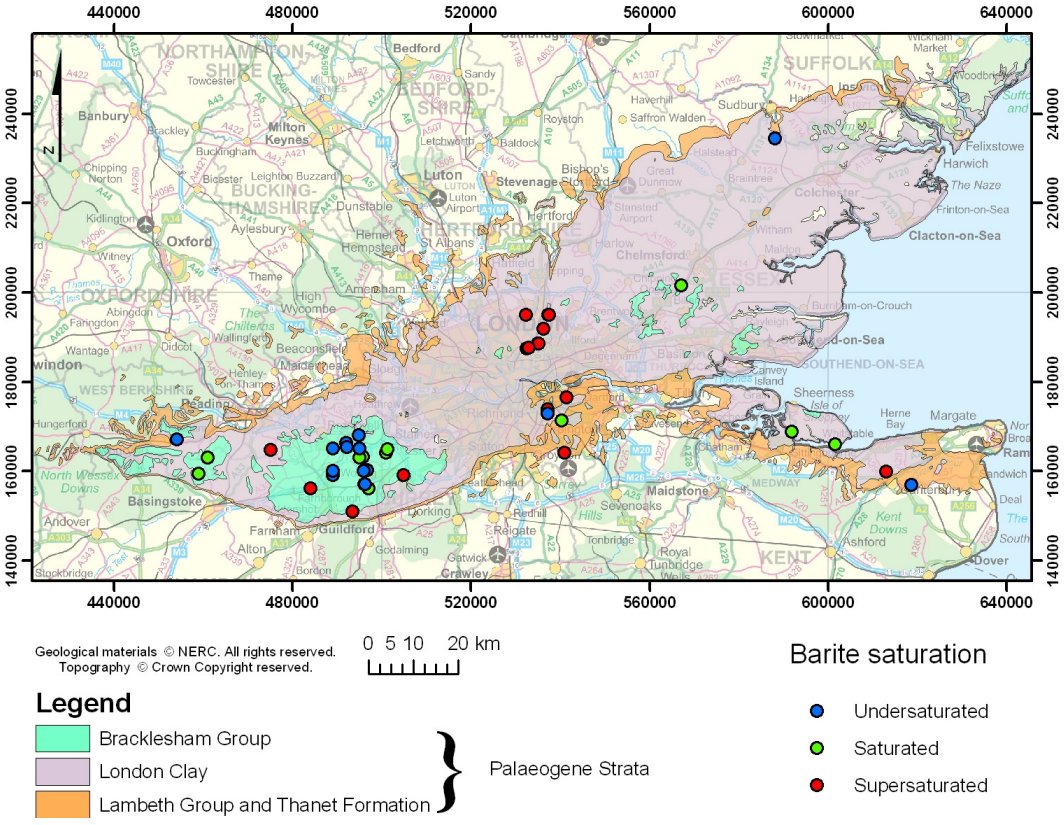

Figure 5.25 Regional variation of barite saturation within the London Palaeogene aquifer

(after Shand et al., 2007). Their distribution is linked to the geology (Figure 5.24), the highest concentrations are generally found in the London Clay and the beds below.

The most likely limiting control on Ba in most groundwaters is saturation with respect to barite ($BaSO_4$) (Hem, 1992). Around half the groundwaters are saturated with respect to barite; most of these are from groundwaters in the beds below the London Clay, whereas most of the groundwaters undersaturated with respect to barite are found in the Bracklesham Group beds (Figure 5.25). Sulphate concentrations of 10 or 100 mg L^{-1} should limit Ba concentration in solution to 140 µg L^{-1} or 14 µg L^{-1} respectively (Hem, 1992). However at SO_4 concentrations of 100 mg L^{-1} Ba is found at concentrations up to 117 µg L^{-1}, indicating there is an additional control over the Ba concentration. Hem (1992) indicated the sorption to metal hydroxides may influence the Ba concentration. However Ba is inversely correlated to Fe, which forms oxides with a very high sorption capacity. The small range is typical of elements controlled by solubility rather than environmental availability, and the scarcity of anthropogenically derived Ba indicates the range is taken to represent baseline compositions.

Strontium has a range of 0.041 to 14.6 mg L^{-1}, a 5th to 95th percentile range of 0.060 to 10.5 mg L^{-1}, and a median of 0.25 mg L^{-1}. This range of Sr in these groundwaters is larger than that of most other sandstone aquifers in England (Shand et al., 2007). The lower values are generally found in groundwaters from the Bracklesham Group beds, and the higher values are found in the London Clay and below. The highest values cluster around the groundwaters taken from the Lea Valley (Figure 5.26). Strontium has similar geochemistry to Ca, and is often found in high concentrations in Ca-bearing minerals. However the spatial distribution does not closely resemble that of Ca (Figure 5.8). In fresh groundwaters there are generally no solubility controls on Sr and it increases according to environmental availability, and

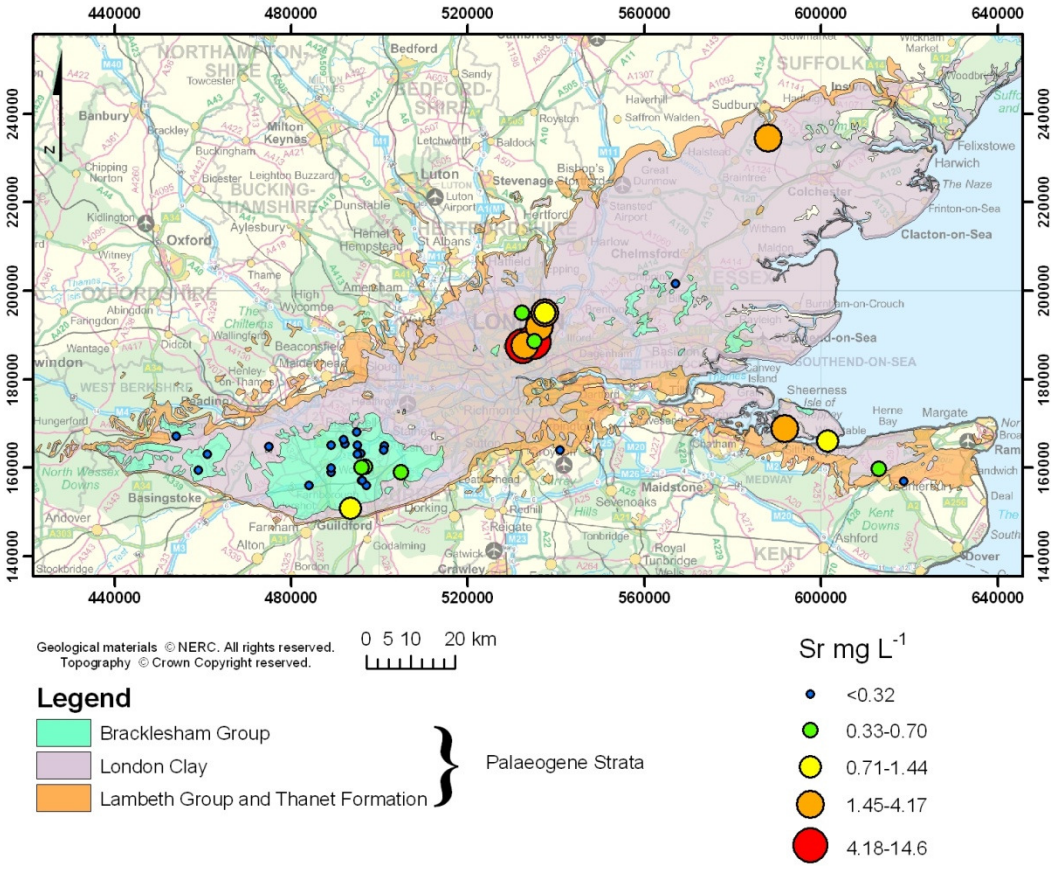

Figure 5.26 Regional variation of Sr within the London Palaeogene aquifer

residence time. Higher ratios of Sr/Ca can be used as an indicator of residence time. Figure 5.27 shows that the highest Sr/Ca ratios are found in the east of the region. These are obtained from samples in the Thanet Formation, which, when confined under the London Clay can represent deeper groundwaters which are likely to be subjected to the longest residence times. The Sr/Ca ratios of samples taken from the Bracklesham Group groundwaters are generally lower and hence likely represent younger groundwaters.

5.2.4 Trace alkali metals

Lithium has a range of <1 to 249 µg L^{-1}, and a median of 18 µg L^{-1}. A 5th percentile is not given in the summary statistics owing to the large number of non-detects, the 95th percentile is 132 µg L^{-1}. This is a typically large range owing to the mobility of Li, which is not easily sorbed (Hem, 1992). There are various detection limits, ranging up to 100 µg L^{-1} making it difficult to distinguish any spatial distribution. There is no notable spatial trend in the detectable concentrations.

Rubidium has a range of 0.92 to 53.4 µg L^{-1}, a 5th to 95th percentile range of 1.31 to 34.4 µg L^{-1} and a median of 3.05 µg L^{-1}. This is a typical range for Rb in UK groundwaters (Shand et al., 2007), and there are no significant spatial concentration trends. Rubidium displays similar geochemical behaviour to K, and in the groundwaters in this study there is a weak positive correlation (r^2=0.3). Rubidium is usually more abundant than Li in the environment, but it tends to sorb more strongly than Li or K at cation-exchange sites, so that Rb is usually only present at low concentrations (Hem, 1992).

Caesium is comparatively rare, it has a range of <0.01 to 1.47 µg L^{-1}, and a median of 0.01 µg L^{-1}. A 5th percentile was not produced in the summary statistics owing to the large number of

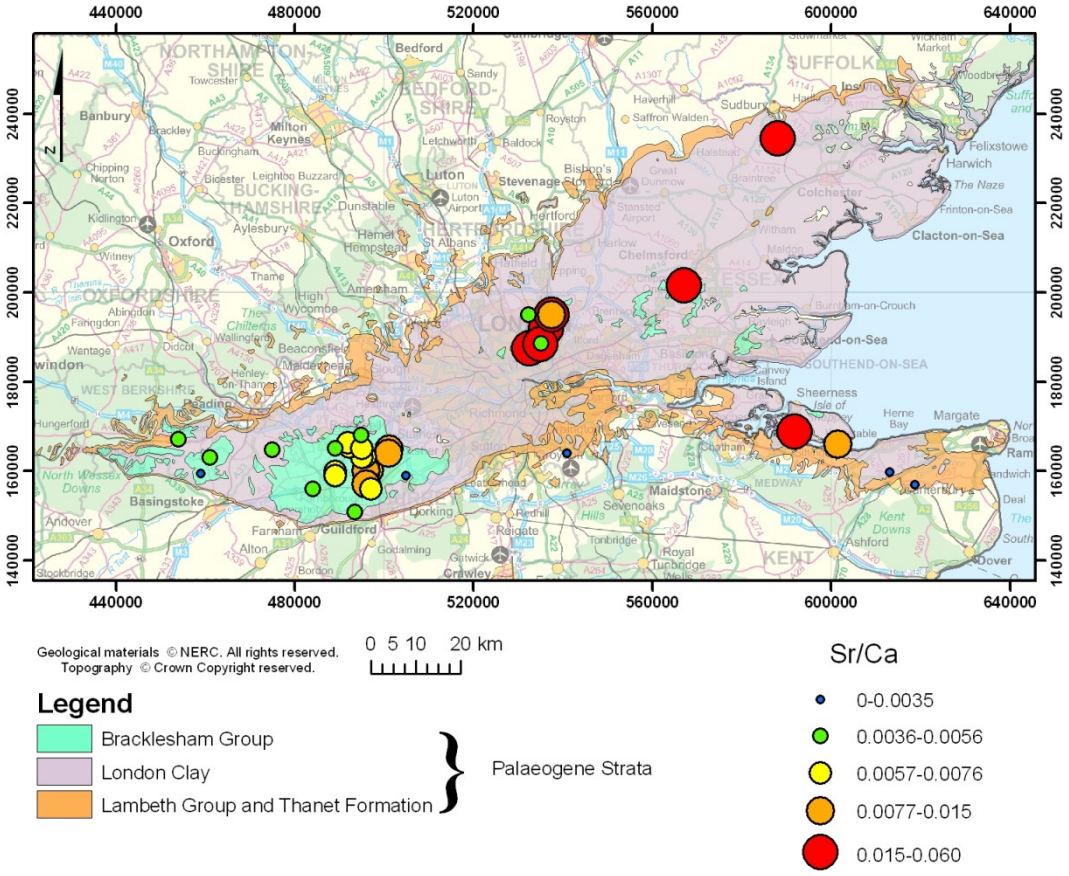

Figure 5.27 Regional variation of Sr/Ca within the London Palaeogene aquifer

non-detects, the 95th percentile is 0.16 µg L^{-1}. Caesium is the rarest stable alkali metal, and it strongly sorbs onto clays, hence the low concentration range. The concentrations presented here are relatively high for Cs, and may derive from the breakdown of feldspar or clay minerals. Any anthropogenically-derived Cs would largely be expected to adsorb in the soil zone and not reach the saturated zone (Shand et al., 2007).

5.2.5 Iron and manganese

Iron and Mn are both redox-sensitive and their abundance and speciation are dependent on local Eh-pH conditions. Iron exists in solution as Fe(II) (reduced) and Fe (III) (oxidised) forms. Iron oxides are soluble under moderately reducing and acidic conditions. Under oxidising conditions Fe(III) prevails. At circum-neutral pH it forms insoluble Fe oxyhydroxides, although in acidic oxic conditions (pH<3, Eh>700mV) Fe^{3+} can be stable in solution (Drever, 1997). Oxidised Fe is also mobile as an organic compound complexed up to pH values of ca. 6. (Langmuir, 1997).

Iron has a range of <0.0005 to 24.8 mg L^{-1}, a 5th to 95th percentile range of 0.006 to 24.2 mg L^{-1}, and a median of 2.1 mg L^{-1}. This is a large range, spanning almost 5 orders of magnitude, and is a greater spread than in most UK aquifers (Shand et al., 2007). The highest Fe concentrations are found in the Bracklesham Group groundwaters (Figure 5.28), although there is a large variability of Fe concentrations within this Group. The Bracklesham Group beds also have the lowest pH values, although the correlation between pH and Fe for the London Palaeogene strata is poor (r^2=0.13). While lower Fe concentrations are found in the Thames Group, Lambeth Group and Thanet Formation, Fe is still present in concentrations

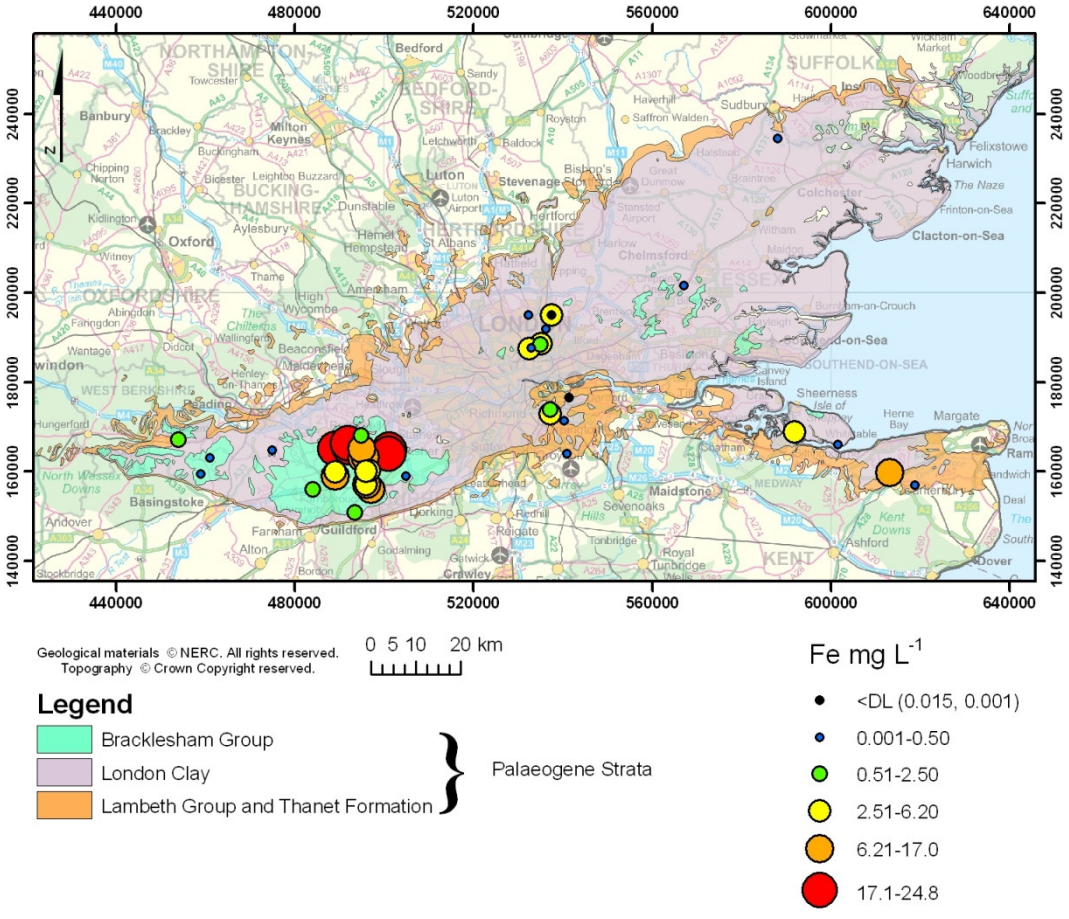

Figure 5.28 Regional variation of Fe within the London Palaeogene aquifer

above the 97.7th percentile of UK aquifers (5.1 mg L^{-1}). The London Palaeogene aquifer contains Fe minerals distributed sporadically throughout (Kinniburgh et al., 1994; Carlile and Dudeney, 2000; Ellison et al., 2004) and there is certainly a large spatial variability caused by this sporadic nature of the Fe minerals present.

The spatial distribution of Fe does not correlate well with that of Eh (Figure 5.4) or SO_4 (Figure 5.13), although Fe is generally found in high concentrations where NO_3-N is low, and in low concentrations where NO_3-N is high. It is interesting to note that the highest Fe concentrations occur in the Bracklesham Group groundwaters, whereas the highest SO_4 concentrations occur in the Thanet Formation groundwaters. This indicates that pyrite is not the only source of Fe. Fluctuating groundwater levels may give rise to dissolution of Fe(III) oxyhydroxides, which in turn may give rise to high Fe concentrations. Additionally iron pans are present in the Bracklesham Group (Ellison et al., 2004), reduction of which may be responsible for the extremely high Fe concentrations in the groundwaters from this aquifer. It is therefore likely that, while pyrite is the primary source of Fe, the secondary minerals give the elevated Fe concentrations in the Bracklesham Group beds. The higher SO_4 values correspond to higher Ca values, and it is possible that these are caused by the dissolution of gypsum, which occurs as a secondary mineral after pyrite oxidation in the presence of calcite (Rainey and Rosenbaum, 1989). A lack of Eh data makes comparison difficult, although where both Eh and Fe data are available there is no correlation ($r^2 = 3 \times 10^{-6}$).

It is a moot point whether the Fe concentrations in the Thanet Formation represent baseline compositions, as the oxidation of pyrite was probably caused, in a large part, by the over

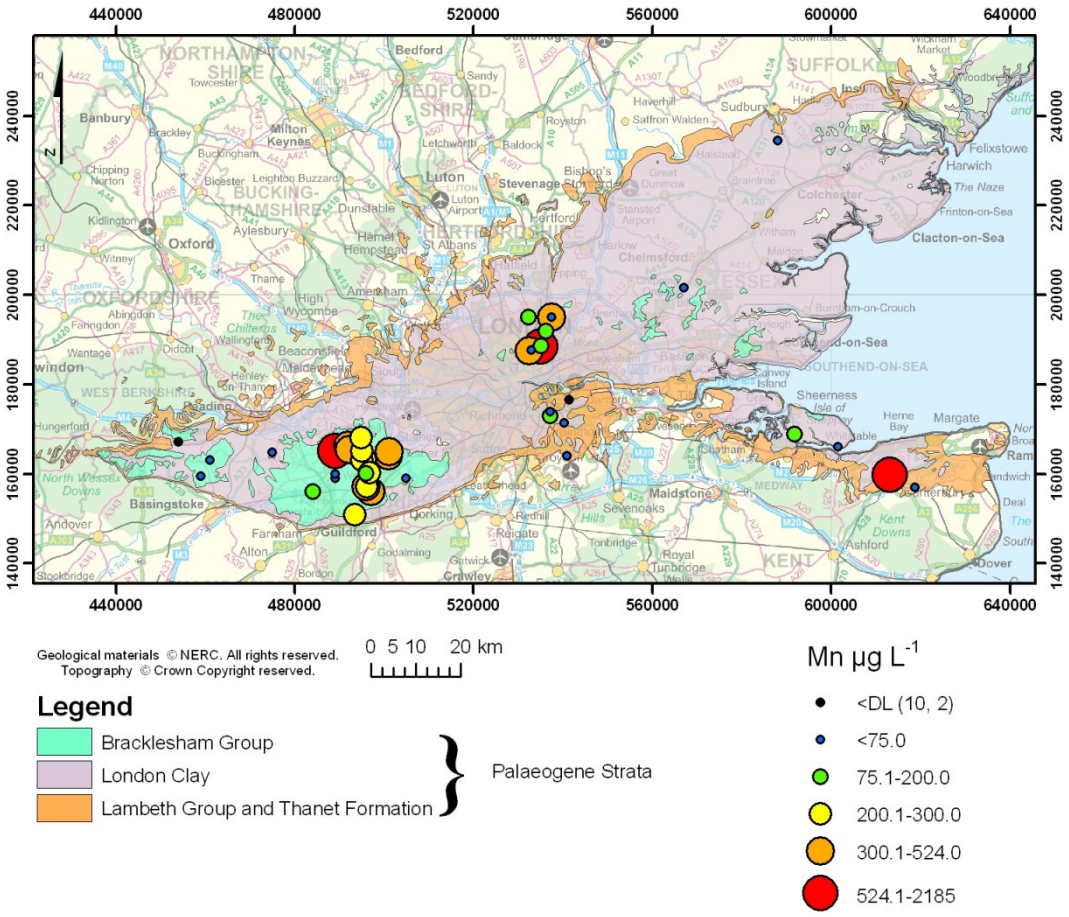

Figure 5.29 Regional variation of Mn within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

pumping of groundwater allowing air access to the previously confined aquifer (see Box 3.1). The higher Fe concentrations are found in Bracklesham Group beds, which have always been open to the atmosphere, meaning there are probably many soluble secondary Fe oxide minerals present. The higher Fe concentrations in these beds represent baseline conditions.

Manganese has a range of <2 to 2180 µg L^{-1}, a 5th to 95th percentile range of 1.5 to 541 µg L^{-1}, and a median of 117 µg L^{-1}. This range is also quite high. Manganese is 50 times less abundant in nature than Fe, and exists in two main oxidation states: Mn(II) and Mn(IV). Under reducing conditions, dissolved Mn will occur as Mn^{2+}, but in contrast to Fe, dissolved Mn remains stable under mildly oxidising conditions. Under fully oxidising conditions Mn precipitates as Mn oxide (Shand et al., 2007). The spatial distribution is sporadic and is similar to that of Fe (Figure 5.29), although the correlation between the two elements (r^2 = 0.06) is poor and there is no correlation with pH ($r^2=2\times10^{-5}$). Manganese oxides are likely to be the main source within the London palaeogene.

5.2.6 Rare earth elements

The rare earth elements (REE) (lanthanides (atomic numbers 57-71)) are, as here, commonly considered as a group along with Y due to their similar behaviour in the environment (Cornell, 1993). The REEs are most commonly below detection limits in groundwaters in the UK (Shand et al., 2007). Quite unusually the REEs determined in this study are mostly detectable, with a maximum concentration of 46 µg L^{-1} (Ce). The maximum concentrations of each REE reflect the Oddo-Harkins rule where even-numbered elements are more abundant than the adjacent odd numbered elements (Faure, 1998).

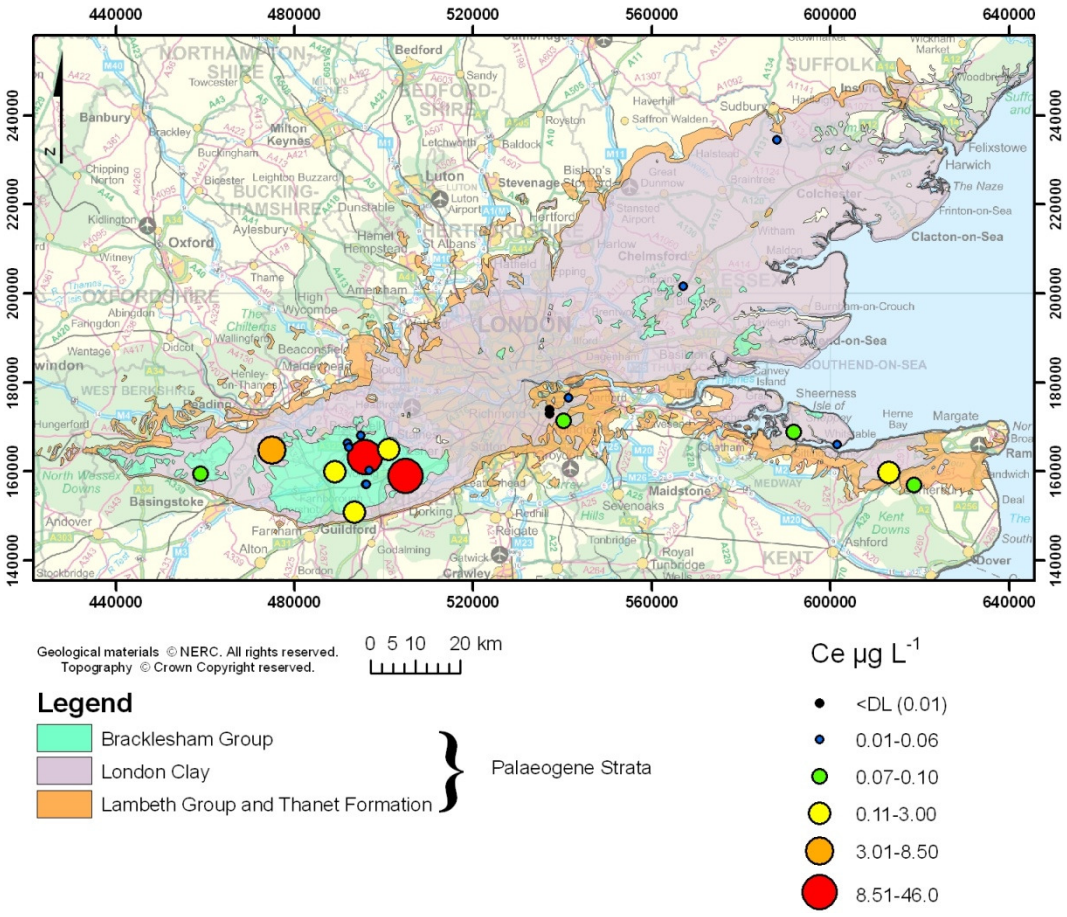

Figure 5.30 Regional variation of Ce within the London Palaeogene aquifer, an example of

The REEs all display a similar distribution within the London Palaeogene beds. Figure 5.30 presents Ce as an example of REE distribution. The highest concentrations are found at selected sites within the Bracklesham Group beds. At least the three highest Ce concentrations are ranked the same for the other REEs, indicating a strong relationship between this group of elements. Rare earth elements display strong sorption characteristics, especially at neutral and high pH, and there is an inverse relationship between pH and REE concentration. The pH control is evident in these samples from the London Palaeogene as the highest concentrations are found in the areas of lowest pH.

5.2.7 Other trace elements

Aluminium has a range of <10 to 766 µg L^{-1}, a 5th to 95th percentile range of 1 to 714 µg L^{-1}, and a median of 10 µg L^{-1}. This is a relatively high concentration range when compared to other UK sandstone aquifers (Shand et al., 2007). Aluminium is one of the most abundant elements in the Earth's crust, but is generally classed as a trace element in natural waters owing to its low solubility around circum neutral pH ranges (pH 6-8). The weathering of aluminosilicates is the dominant source of Al to natural waters (Shand et al., 2007), and it seems as if the range presented here represents baseline as the highest Al concentrations are found where the pH is lowest, below the circum-neutral range, where Al is soluble (Figure 5.31, see also Figure 5.3. It appears the Al is most likely derived naturally from aluminosilicate minerals, but as there are few data within Greater London it is difficult to identify an anthropogenic signature.

Arsenic has a range of <0.05 to 6.36 µg L^{-1}, and a median of 0.29 µg L^{-1}. This is slightly

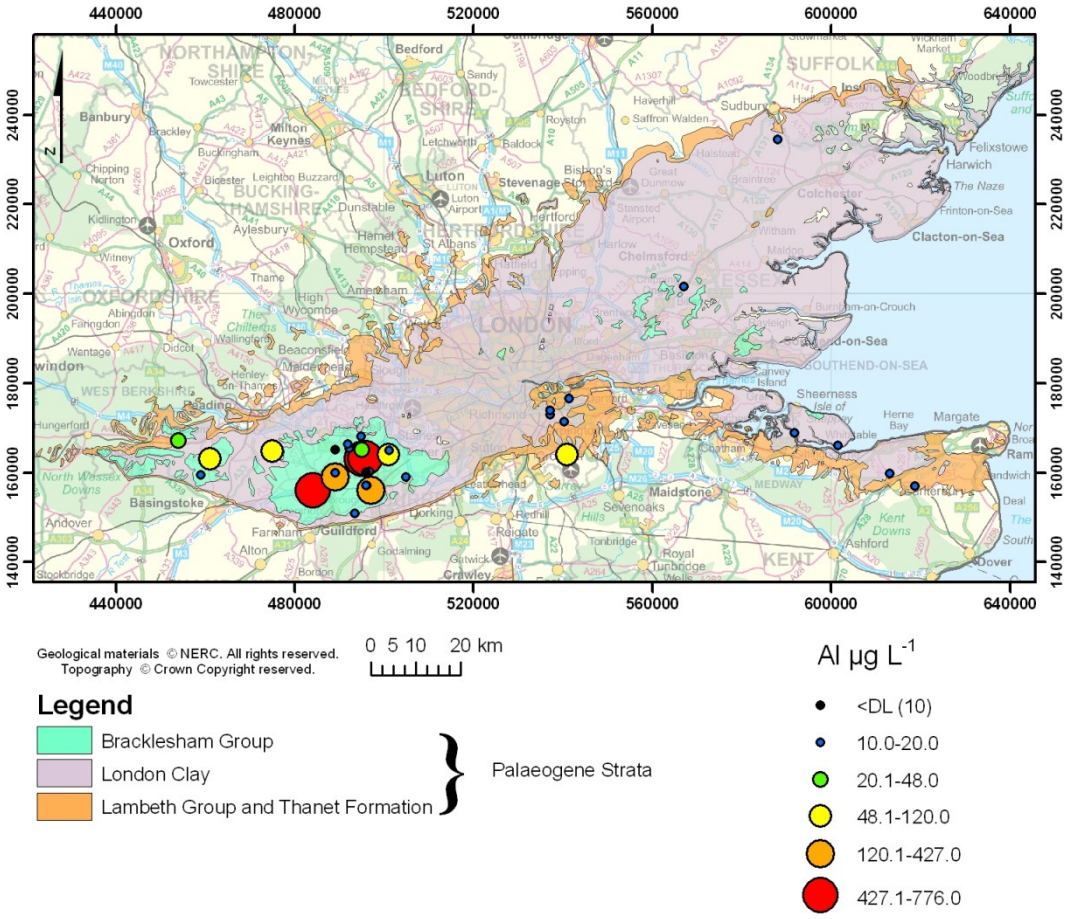

Figure 5.31 Regional variation of Al within the London Palaeogene aquifer

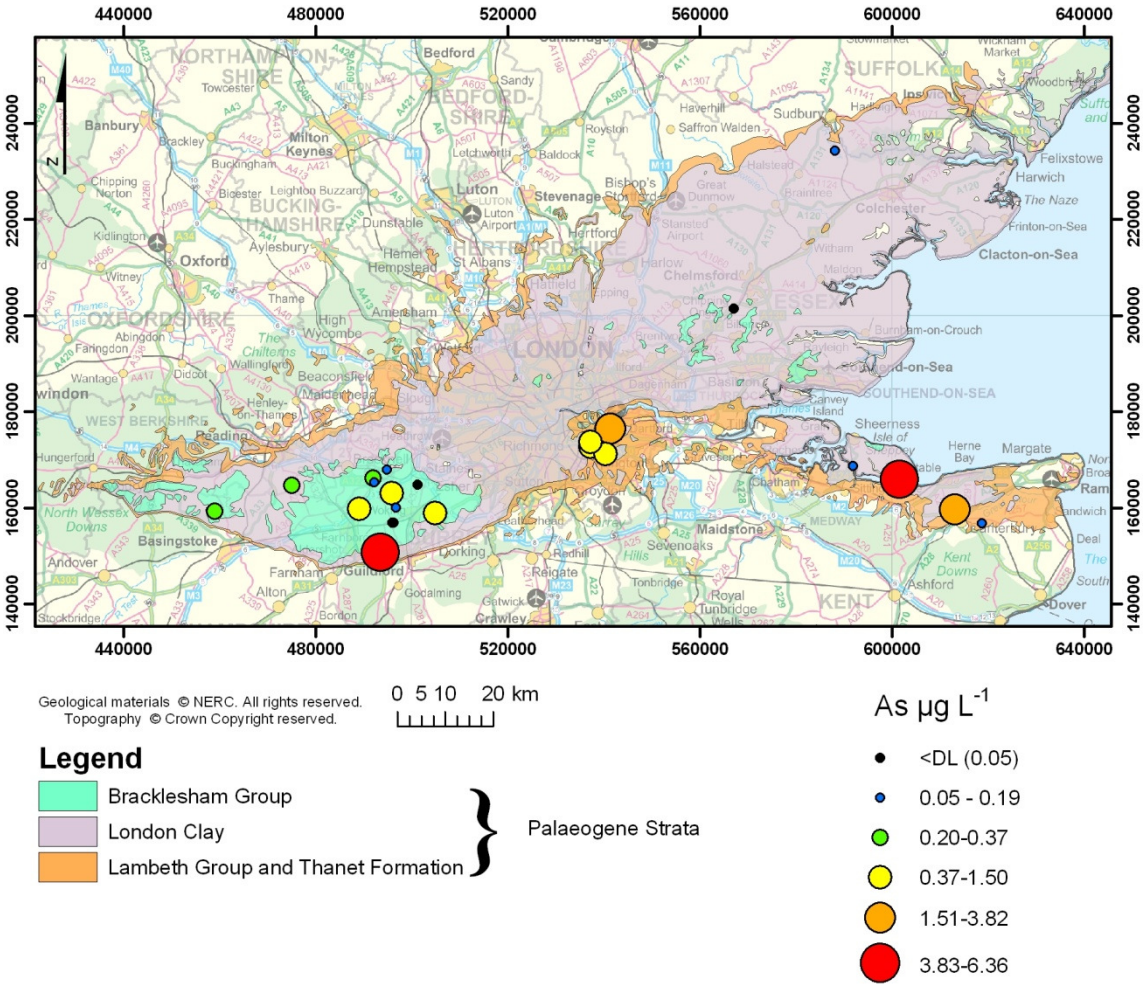

Figure 5.32 Regional variation of As within the London Palaeogene aquifer

below the range reported for other UK sandstones (after Shand et al., 2007). While the highest concentrations are upper outliers distinct from the main data set, all waters are well within the 10 µg L^{-1} limit for drinking water (OPSI, 2000). Arsenic has two main oxidation states in groundwater, As(III) and As(V). The As(III) form is typically the dominant form in Fe reducing conditions. As(V) is strongly sorbed to metal oxides at near-neutral and high pH values, and hence under oxidising conditions the concentrations of dissolved As are expected to be low. It is interesting to note therefore, that while there is little clear spatial distribution, the highest As concentrations are found in two sites where the groundwater is oxidising and circum neutral (Figure 5.32). The reason for this is unclear, and there are no obvious sources of As contamination at either of these sites. Pyrite is considered the most likely source of this As.

Boron has a range of <10 to 801 µg L^{-1}, and a median of 57 µg L^{-1}. This is a wide range of B concentrations, which is typical of sandstone aquifers in England (Shand et al., 2007). Almost one third of the analyses are below the detection limit, however many of these correspond to a detection limit that is greater than detected values. The lowest concentrations are generally found in the Bracklesham Group, and the highest are found in the central portion of the Thanet Formation (Figure 5.33). This is at the centre of the syncline and where the boreholes are deeper. The shallower boreholes on the periphery of the Palaeogene outcrop are generally of moderate concentration. Boron is associated with iron oxides and clays, which may be a source in these groundwaters. Additionally the seawater concentration is relatively high (ca.

4.5 mg L^{-1}) meaning seawater intrusion, mixing with formation waters or ion exchange can be a source of B.

Beryllium has a range of <0.005 to 1.1 µg L^{-1}, a 5th to 95th percentile range of 0.002 to 0.65 µg L^{-1}, and a median of 0.02 µg L^{-1}. Over half of the analyses are below detection limit. However, as with B, many of these correspond to a detection limit that is greater than most of the determined values. Beryllium is generally present at concentrations below 1 µg L^{-1} in UK groundwaters, and commonly below detection limit, so the distribution seen here is not unusual. From the limited data it seems that the highest concentrations are found within the Bracklesham Group.

Cadmium has a range of <0.01 to 1.05 µg L^{-1}, a 5th to 95th percentile range of 0.0002 to 0.24 µg L^{-1}, and a median of 0.01 µg L^{-1}. In UK aquifers it is usual for Cd median concentrations to be below detection limit and the concentration rarely exceeds 1 µg L^{-1} (Shand et al., 2007). Over half of the analyses in this study are below detection limit; there are multiple detection limits, which mostly exceed determined concentrations. There is one large outlier at 1.05 µg L^{-1}, and the second highest value is 0.27 µg L^{-1}. It is difficult to define any spatial trends as there are few data points and the non-detects are evenly distributed. It is possible therefore that the anomalous value is due to contamination, which can be derived from high-Cd phosphate fertilizers or sewage sludge applications. The maximum concentration was found in groundwaters at a greenhouse complex near Farley Hill.

Cobalt has a range of <0.02 to 21.9 µg L^{-1}, and a median of 1.1 µg L^{-1}. This is a relatively

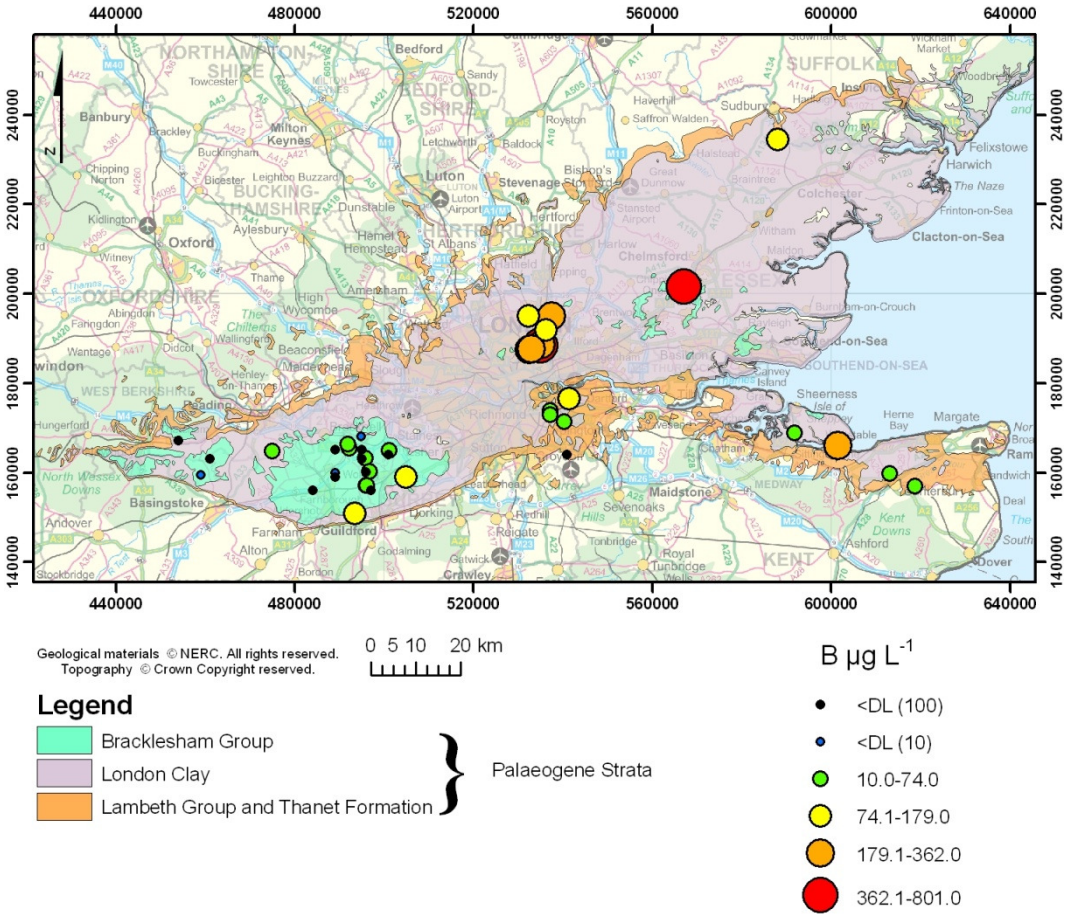

Figure 5.33 Regional variation of B within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

large range when compared to other sandstone aquifers in England. Six out of 34 analyses are above 10 µg L^{-1}, which is considered to be the upper limit of baseline in other groundwaters in England and Wales (Shand et al., 2007). Cobalt is commonly found associated with Fe and/or Mn, suggesting this element may be controlled by sorption and dissolution reactions involving oxyhydroxides. Sorption limits the mobility of Co in high pH waters (Shand et al., 2007). The spatial distribution of Co (Figure 5.34) is comparable to Fe (Figure 5.28) and is strongly linked to pH (Figure 5.3), there is a moderate correlation between pH and Co (r^2=0.4). The highest values are all found in Bracklesham Group groundwaters, apart from one, which is in Thanet Formation groundwater near Canterbury. This strong relationship with pH and Fe implies that, despite the elevated concentrations the Co in the London Palaeogene aquifer represents a baseline composition.

Chromium has a range of <0.03 to 1.91 µg L^{-1}, a 5th to 95th percentile range of 0.009 to 1.17 µg L^{-1}, and a median of 0.1 µg L^{-1}. Over half the analyses are below detection limit and there are multiple detection limits, which mostly exceed measured analyses. Only three analyses, out of 34 exceed 1 µg L^{-1}. This range of Cr is smaller than that of most other sandstone groundwaters in England. There is no clear spatial distribution, despite the geochemical behaviour of Cr being controlled by Eh and pH (Shand et al., 2007).

Copper has a range of <0.5 to 89.2 µg L^{-1}, a 5th to 95th percentile range of 0.06 to 81.3 µg L^{-1}, and a median of 1.8 µg L^{-1}. This is a typical distribution in sandstone groundwaters in England. Copper occurs naturally as native metal, or in sulphide ore deposits, but is also a very commonly used metal in industrialised countries. Anthropogenic inputs are to be expected in young groundwaters (Shand et al., 2007). Where the groundwater is oxidising, Cu

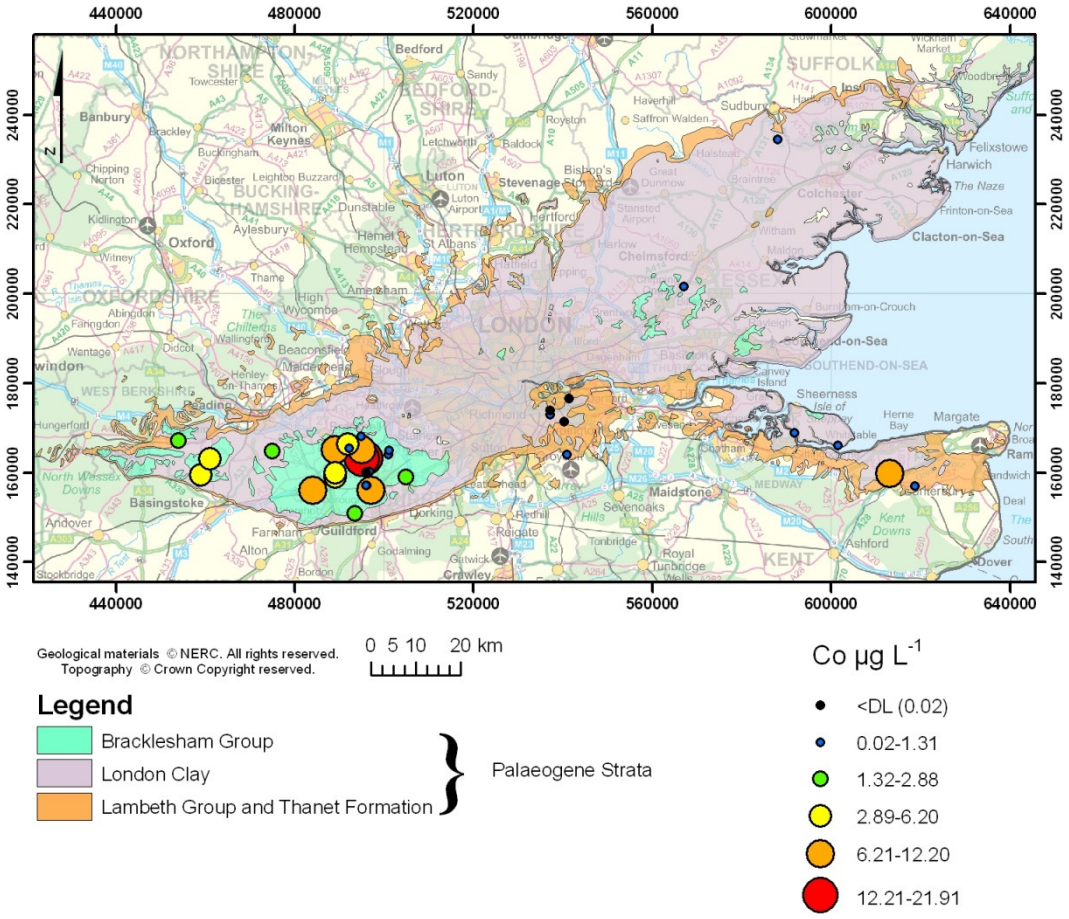

Figure 5.34 Regional variation of Co within the London Palaeogene aquifer

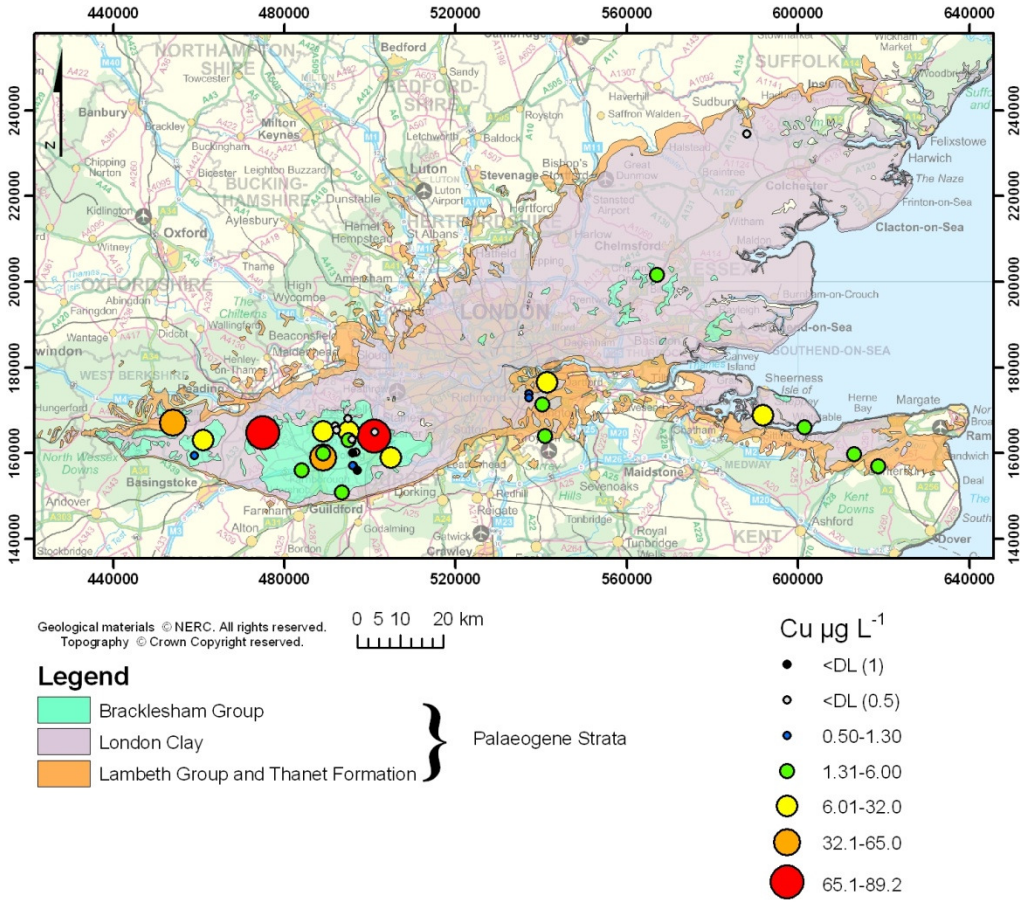

Figure 5.35 Regional variation of Cu within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

is most soluble under acidic conditions. As the pH increases, Cu can become adsorbed to organic matter or Fe and Mn oxyhydroxides. The spatial trend in the London Basin is ambiguous. The highest concentrations appear to be found in the Bracklesham Group groundwaters (Figure 5.35), correlating to the lower pH values, yet many of the non-detects are found in close proximity. There is a poor correlation between pH and Cu (r^2=0.02). This could indicate contamination derived from many anthropogenic activities.

Molybdenum has a range of <0.2 to 5.2 µg L^{-1}, a 5th to 95th percentile range of 0.01 to 4.7 µg L^{-1}, and a median of 0.13 µg L^{-1}. This is a typical range of Mo in groundwaters from sandstone aquifers in England, which rarely exceed 10 µg L^{-1} (Shand et al., 2007). Over half the analyses are below detection limit and the detection limit exceeds some measured analyses. The dominant Mo species is pH dependent (Shand et al., 2007), and Mo distribution in the London Palaeogene groundwaters (Figure 5.36) is linked to pH (see Figure 5.3) and geology (see Figure 3.1). Within the Bracklesham Group groundwaters the concentration of Mo is generally below detection, with only one sample containing Mo at the limit of detection. The remaining measurable Mo is found in groundwaters from the London Clay, Lambeth Group and Thanet Formation.

Nickel has a range of <0.2 to 40.6 µg L^{-1}, a 5th to 95th percentile range of 0.07 to 37.4 µg L^{-1}, and a median of 2.7 µg L^{-1}. This range is similar to the Ni concentrations in other English sandstone aquifers. Ni is geochemically similar to Co, which associates with Fe; the Ni spatial distribution (Figure 5.37) is similar to that of Co (Figure 5.34) and hence also Fe (Figure 5.28). There is also a moderate correlation with pH (r^2=0.38). This strong geochemical relationship to geology implies that these concentrations represent baseline, except possibly

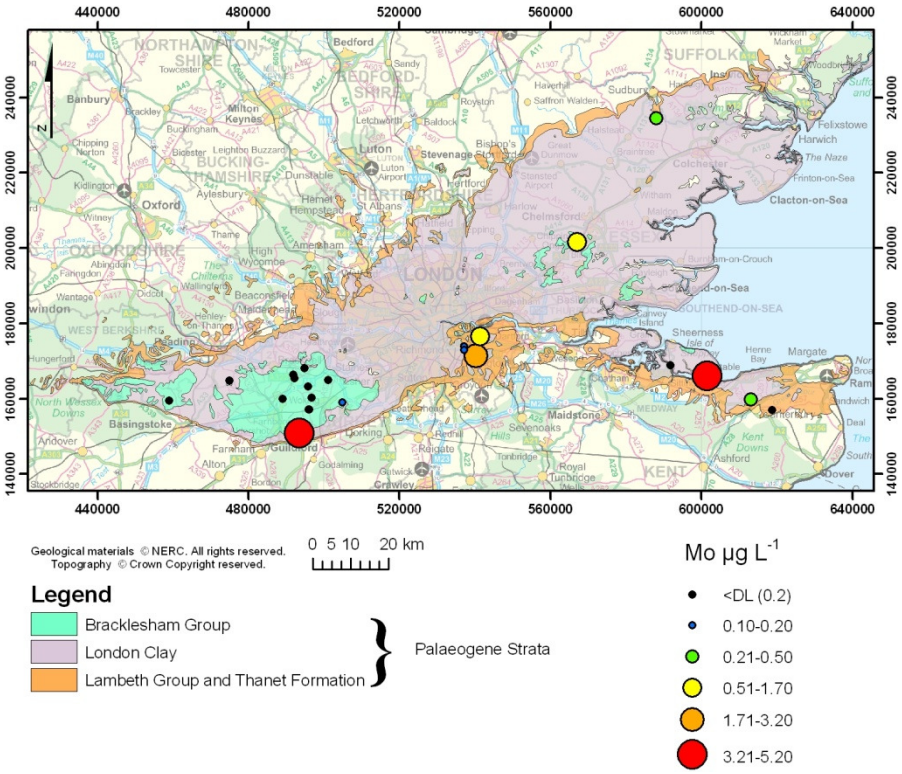

Figure 5.36 Regional variation of Mo within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

where elevated concentrations occur in the Thanet Formation and are therefore affected by groundwater abstraction. Nickel is present in some of the groundwaters at concentrations that exceed the drinking water level of 20 µg L^{-1} (OPSI, 2000).

Lead has a range of <0.1 to 13.3 µg L^{-1}, a 5th to 95th percentile range of 0.002 to 4.7 µg L^{-1}, and a median of 0.08 µg L^{-1}. Over half the Pb analyses are below detection, most of the concentrations are low, for example the 75th percentile is 0.45 µg L^{-1}, although there are some upper outliers (see Figure 5.18). The Pb relationships are similar to those of Ni and Cu, suggesting the Pb is controlled by pH, although the relationship between pH and Pb is very poor (r^2= 0.019). There are limited measurable analyses. However all samples >0.5 µg L^{-1} Pb are found within close proximity (≤2 km) of motorways or major A roads, and in unconfined areas of the aquifer. The natural baseline of Pb is likely to have been affected around built up and industrial areas, and major roads owing to anthropogenic influences. While there were some high Pb values around the road network, those below the arbitrary value of 0.47 µg L^{-1} could be considered baseline in these groundwaters. All except one determination fall below the drinking water limit of 25 µg L^{-1}, and the drinking water limit of 10 µg L^{-1}, which is effective as of 25th December 2013.

Antimony has a range of <0.005 to 1.27 µg L^{-1}, and a median of 0.01 µg L^{-1}. Antimony rarely exceeds 0.1 µg L^{-1} in English sandstone groundwaters (Shand et al., 2007). Over half the analyses are below detection with respect to Sb, and there are multiple detection limits meaning that some of the detection limits are greater than measured values. While it is difficult to define spatial trends owing to these multiple detection limits, it can be seen that the highest values are found in the London Clay and the more southerly Thanet Formation groundwater samples. Antimony is typically present at <1 µg L^{-1} in unpolluted waters (Shand et al., 2007). Only one determination exceeds this. This maximum concentration was measured in the London Clay groundwater.

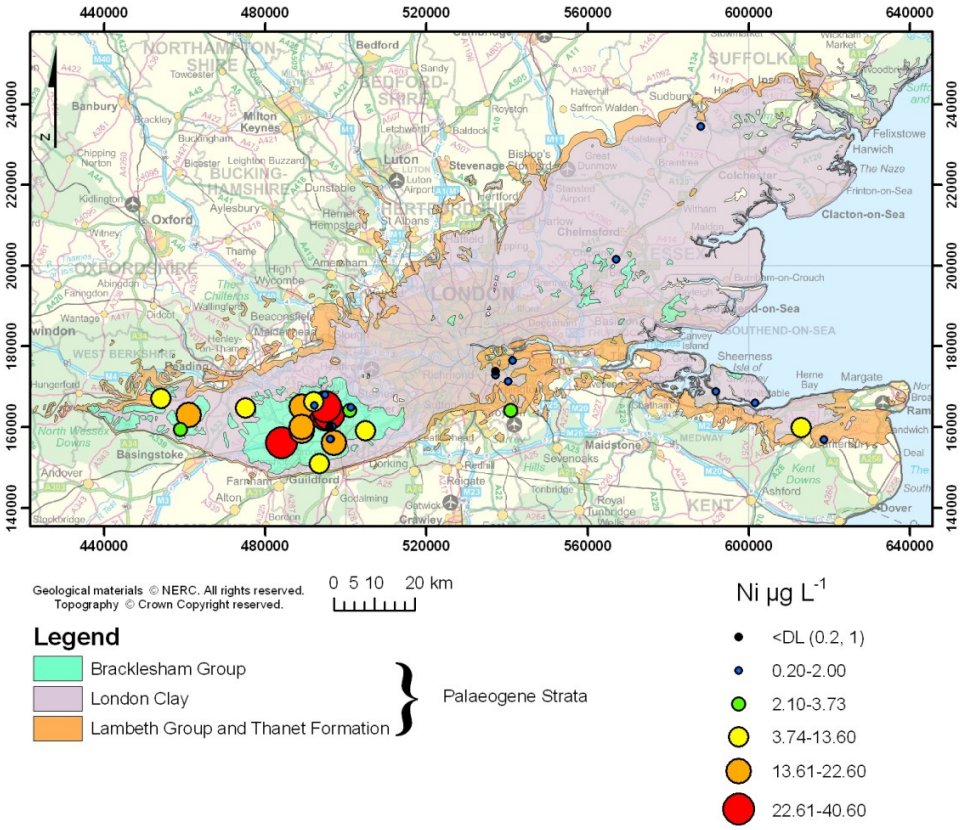

Figure 5.37 Regional variation of Ni within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

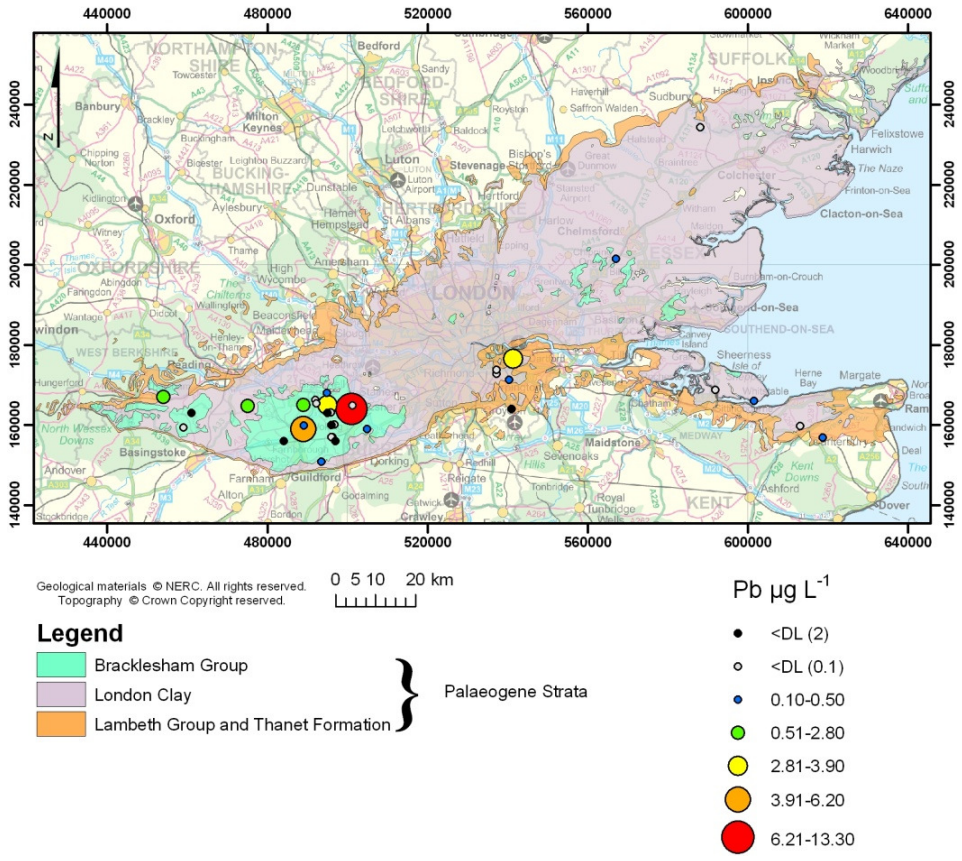

Figure 5.38 Regional variation of Pb within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

Selenium has a range of <0.01 to 4.5 µg L^{-1}, a 5th to 95th percentile range of 0.01 to 1.3 µg L^{-1}, and a median of 0.03 µg L^{-1}. Selenium is a relatively rare element, it is present in oxidising waters, but in confined conditions it is readily reduced to elemental, and relatively insoluble, Se. Where Fe is present Se may be co-precipitated or sorbed (Hem, 1992). With its low abundance and limited mobility Se concentrations are expected to be low in natural waters, indeed analyses of US groundwaters and surface waters showed that Se rarely exceeded 1 µg L^{-1}. Higher concentrations have been found in shallow saline groundwaters affected by irrigation drainage, and higher values were found where there were higher dissolved solids concentrations (Hem, 1992).

There are limited Se analyses, but it is clear that the lowest concentrations are found in the Bracklesham Group beds, and the highest are found in the groundwaters of underlying formations (Figure 5.39). Selenium may be associated with pyrite, and oxidation of sulphide minerals can release Se, although desorption from Fe and Al oxides is also possible (Stuart and Smedley, 2009). Elevated Se concentrations may also be caused by a saline influence at sites proximal to the coast. Selenium has been found in the groundwater in the Chalk aquifer underlying the Palaeogene in the Hampshire Basin at concentrations of up to 30 µg L^{-1}, which is assumed to derive from the overlying Palaeogene (Stuart and Smedley, 2009). The likely source of such a large concentration of Se, which is not evident in any of the samples in this study would be pyrite. In this study two out of 23 analyses exceeded 1 µg L^{-1}. The largest value of 4.5 µg L^{-1} was measured in groundwater taken from a borehole near the coast on the Isle of Sheppey, this corresponds to a relatively large SO_4, but small Fe concentrations,

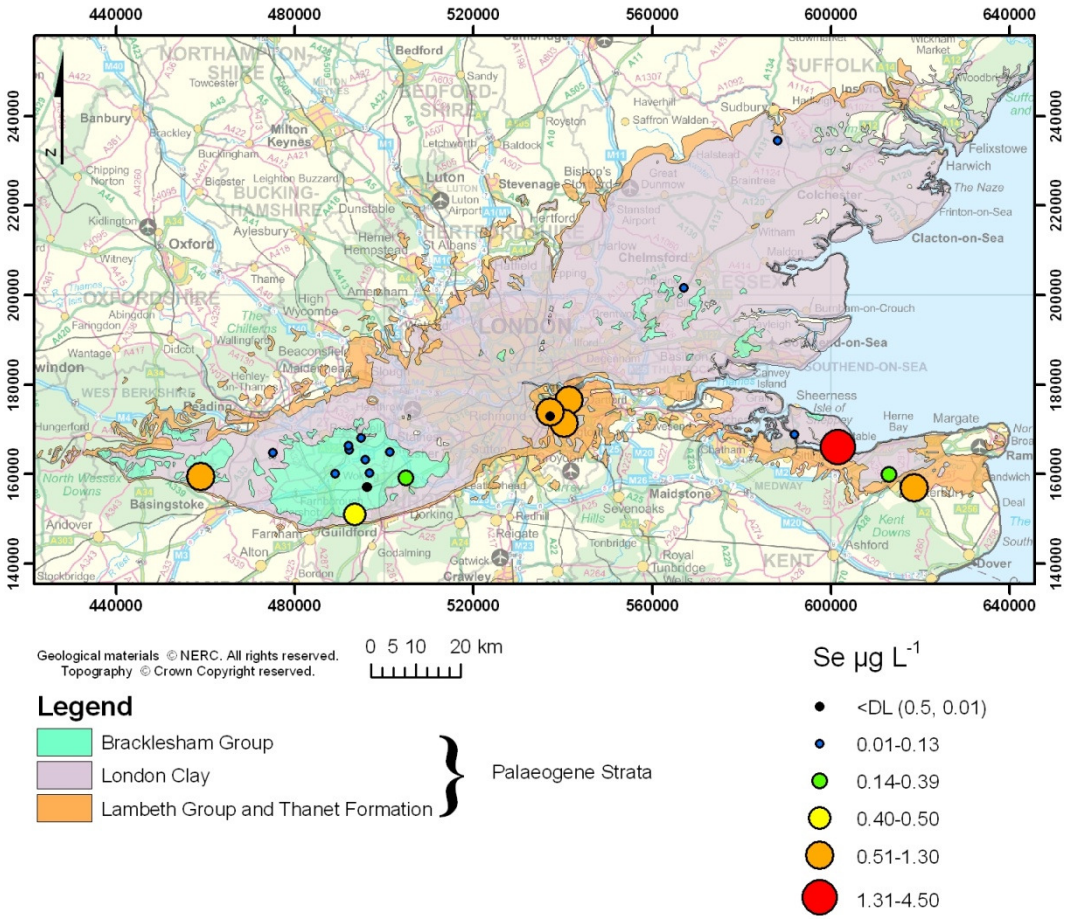

Figure 5.39 Regional variation of Se within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

indicating pyrite is unlikely to be the source at this site. Selenium has shown a strong correlation with NO_3 in groundwaters owing to the presence in N-rich fertilisers (Gates et al., 2009). The highest Se value in this study correlates to a high NO_3-N, meaning the addition of fertilisers may also be a potential source. It is likely that the values above 1 µg L^{-1} do not represent baseline.

Tin has a range of <0.1 to 1.5 µg L^{-1}, and a median of 0.1 µg L^{-1}. Almost half of the analyses are below detection limit. While the maximum value is unusual, the range is typical of groundwaters from sandstone aquifers in England (Shand et al., 2007). The spatial distribution does not correspond to the geology, or form any other spatial trends. The maximum concentration is found at a site towards the north of the Bracklesham Group outcrop, and it is likely that it represents contamination. The second highest Sn concentration is found in the ground water in the sample taken from the London Clay. This site has elevated concentrations in numerous elements (see above descriptions), which may be derived from the Clay.

Titanium has a range of <0.1 to 6.6 µg L^{-1}, and a median of 1.4 µg L^{-1}. Almost half of the analyses are below detection limit. While Ti is relatively abundant in crustal rocks, it is generally found in resistant minerals, which means its abundance is low in natural waters. Titanium can range up to a few tens of µg L^{-1}, and averages 3 µg L^{-1} in stream waters (Hem, 1992). All analyses except one are below 3 µg L^{-1} (the largest determination is 6.6 µg L^{-1}) and may represent contamination given the low concentrations in the majority of the samples.

Uranium has a range of <0.005 to 4.65 µg L^{-1}, a 5th to 95th percentile range of <0.005 to 3.52 µg L^{-1} and a median of 0.013 µg L^{-1}. This distribution is typical of the groundwaters of most sandstone aquifers in England, but has a smaller concentration range than the Permo-Triassic sandstones and the median is lower than the average median for major aquifers in England and Wales (0.27 µg L^{-1}) (Shand et al., 2007). The spatial distribution is fairly even, although the highest concentrations are towards the south of the Palaeogene outcrop (Figure 5.40). Uranium mobilisation is strongly controlled by its redox state. It is usually only the oxidised form (U(VI)) that occurs significantly in solution (Smedley et al., 2006). Where there are reducing conditions, the concentration of U is generally low, indeed the most oxidising waters are found to the south of the Palaeogene outcrop area (Figure 5.4). Uranium occurs naturally in soils and rock-forming minerals, and it is likely that the source of U in these waters is derived from the London Clay as such argillaceous rocks are known to contain appreciable quantities of U (Smedley et al., 2006). All of the determinations are well within the WHO provisional drinking water guideline value of 15 µg L^{-1} , and is unlikely that the observed concentrations of U are impacted significantly by anthropogenic inputs.

Vanadium has a range of <0.01 to 12.3 µg L^{-1}, a 5th to 95th percentile range of 0.003 to 3.09 µg L^{-1} and a median of 0.07 µg L^{-1}. Median baseline concentrations of aquifers in England and Wales are less than 1 µg L^{-1}, with maximum concentrations reaching around 30 µg L^{-1} (Shand et al., 2007). In this study the concentrations are generally < 1 µg L^{-1}, with the exception of three sites towards the south of the Palaeogene outcrop. The two sites with the largest V concentration have been commented upon above: the site within the London Clay and the coastal site on the Isle of Sheppey. Vanadium is highly mobile under oxidising and circum neutral conditions, and these two sites fulfil these criteria. It is possible that the concentrations in this study represent baseline compositions.

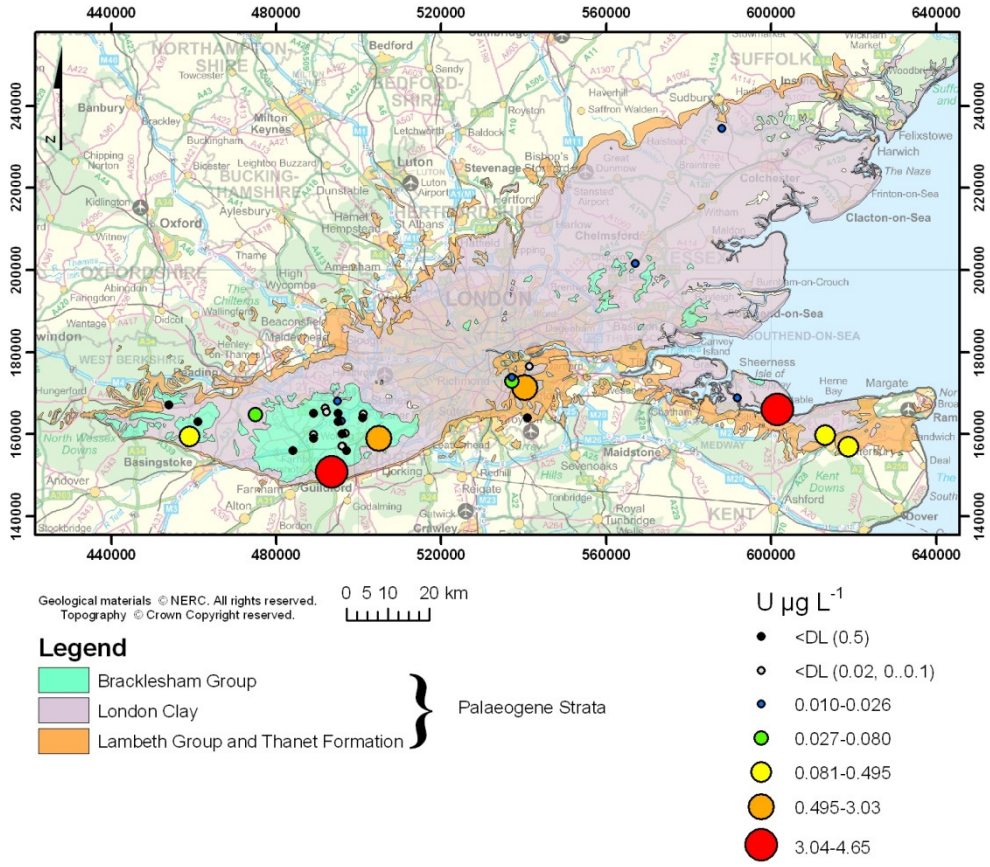

Figure 5.40 Regional variation of U within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

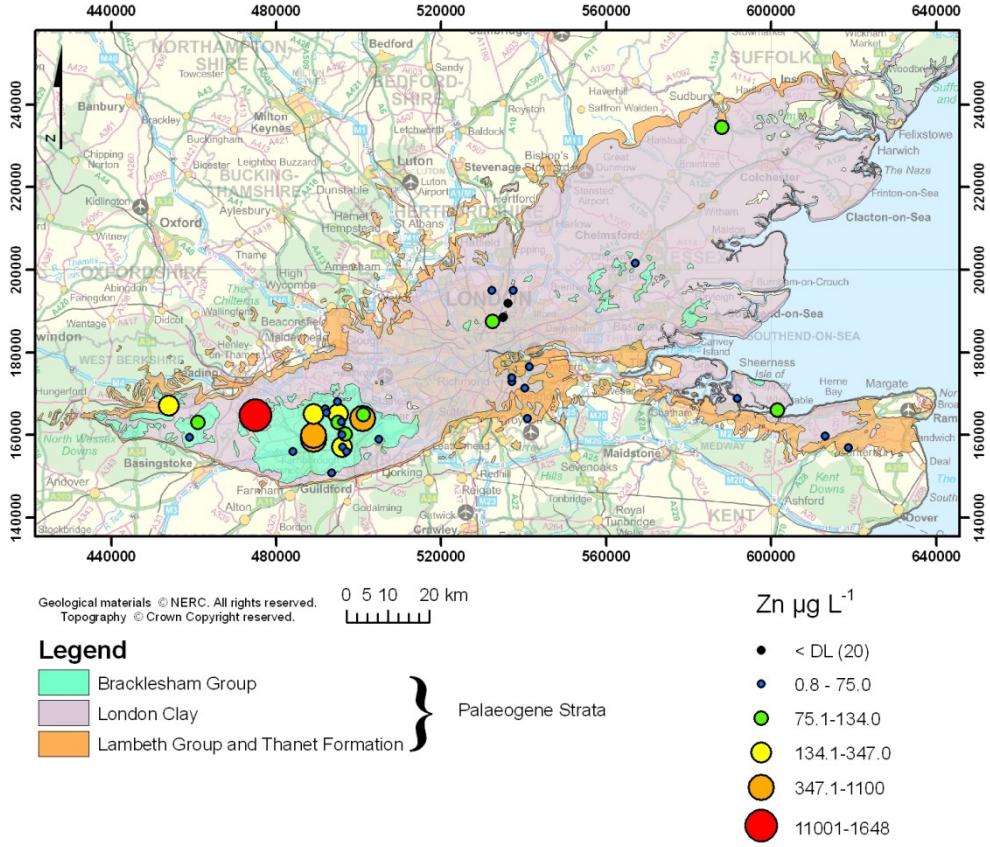

Figure 5.41 Regional variation of Zn within the London Palaeogene aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

Zinc has a range of <20 to 1650 µg L^{-1}, a 5^{th} to 95^{th} percentile range of 1.5 to 952 µg L^{-1}, and a median of 43 µg L^{-1}. This is a fairly large range, but it is comparable with the ranges of Zn in other sandstone groundwaters in England and Wales (Shand et al., 2007). The highest concentrations are all found within the Bracklesham Group groundwaters (Figure 5.41), although there are very low concentrations within close proximity. As this is a densely populated area with a well developed road network it is possible that the higher values represent contamination derived from road dust, landfill leachate, or other urban contamination sources. However the solubilities of some Zn minerals are high, meaning Zn is expected in groundwaters to be more widespread and present at higher concentrations than other transition metals. There is a moderate correlation with Cu (r^2=0.55), but a poor correlation with pH (r^2 = 0.07). This indicates that while pH may control the natural concentration, many of the higher Zn concentrations may be associated with contamination.

5.3 SITES OF PARTICULAR INTEREST

The above discussion has highlighted two broad populations: the Bracklesham Group groundwaters and those in the underlying Thames Group, Lambeth Group, and Thanet Formation. The Bracklesham Group groundwaters are young and are directly recharged. The underlying beds receive their recharge from the periphery of the Palaeogene outcrop, or upwelling from the underlying chalk. This physical difference, and hence the variable mineral interactions may play a role in determining the groundwater chemistry in the London Palaeogene groundwaters.

The physico-chemical parameters of the groundwaters within the Palaeogene can also be divided into the same populations. The Bracklesham group generally has lower pH, and SEC, than the underlying Thames Group, Lambeth Group, and Thanet Formation. The Eh, however does not follow this trend, and varies greatly within close proximity in all Palaeogene beds. As it is the interdependence of pH and Eh which determine the distribution of many inorganic constituents it is unsurprising to find that while many determinands can also be divided into the two populations, the sporadic nature of the Eh means that there are variations within each population.

Additionally there are a few sites worthy of note, this is either because of the unique site geology (only one sample was taken from the London Clay), the impact of the landuse, or because there are anomalous concentrations of some elements.

The only groundwater abstracted from the London Clay was sampled from a well at farm in Normandy, near Guildford. The sample was taken using the small caravan pump as the well had been disused for many years. Given the size of the bore (ca 1.5 m in diameter) it was impossible to pump out three times the well volume to obtain a fresh sample. The sample has one of the highest SECs and consequently contains elevated levels of many elements. It is unclear whether the solute content is naturally derived and representative of the London Clay as this was the only sample from the formation. The London Clay is generally considered an aquiclude, hence it is only locally exploited for small quantities of groundwater and there are no other London Clay sites for comparison.

The site by the coast on the Isle of Sheppey contains elevated concentrations of selected trace elements (e.g. Mo, Se, and U) where the other samples taken along the Kent coast (also from the Thanet Formation) contain comparatively low concentrations. These three elements can all be found in fertilisers (Smedley et al., 2006; Smedley et al., 2008; Gates et al., 2009), and are found in conjunction with elevated concentrations of nutrient species (NO_3-N, and K) in the groundwater. There is arable farming in this low-lying flat area (see Figure 2.2) and fertilizer inputs could cause these elevated concentrations.

At one site near Woking the groundwater has the chemistry of a contaminated sample. It has a neutral pH, relatively high conductivity, and high concentrations of K, Cl, SO_4, NO_3-N, NO_2-N, NH_4, DOC and B. These elevated concentrations may indicate agricultural pollution. The borehole, situated in the centre of a field was rarely pumped and the water was used for irrigation. In the groundwater sampled from this site there were low concentrations of Fe and Mn, and measurable U, which all suggest this is an oxic groundwater. In contrast there are high REE concentrations. The Eh and DO were not measured at this site as the water could only be sampled from the head of a spray irrigation system, and the water was consequently artificially aerated.

A site near Ascot shows strongly reducing conditions. The measured Eh is -59mV, and it appears that the reduction is sufficient to cause SO_4 reduction, and nitrate reduction. This is evidenced by a low SO_4 concentration (0.215 mg L^{-1}), a low NO_3-N concentration (0.23 mg L^{-1}), and a corresponding high NH_4-N concentration (6.7 mg L^{-1}). This groundwater represents the most reducing sample taken in this study. The proximity to fully oxidised groundwaters reflects the varied conditions of the groundwaters within the Bracklesham Group beds.

5.4 ISOTOPIC COMPOSITION

Measured compositions of $\delta^{18}O$ lie in the range -8.01 to -6.59 ‰ with a median of -7.11 ‰. The $\delta^{2}H$ has a range of -55.1 to -40.9 ‰ with a median of -46 ‰. The range of compositions is large, reflecting the large study area. The interquartile ranges of $\delta^{18}O$ and $\delta^{2}H$ are generally consistent with compositions of recently recharged (Holocene) groundwaters analysed from south-west England (Darling et al., 2003). Values within the upper and lower 25th percentiles of the $\delta^{18}O$ and $\delta^{2}H$ data are outside of the range of values expected for local Holocene groundwaters, and more negative values may represent older groundwaters (Darling et al., 2003). However, the relationship between $\delta^{18}O$ and $\delta^{2}H$ (Figure 5.42) shows a general correspondence with the world meteoric water line, indicating that the groundwaters represent recharged local modern rainfall. The $\delta^{18}O$ and $\delta^{2}H$ data are distinguished in Figure 5.42 by

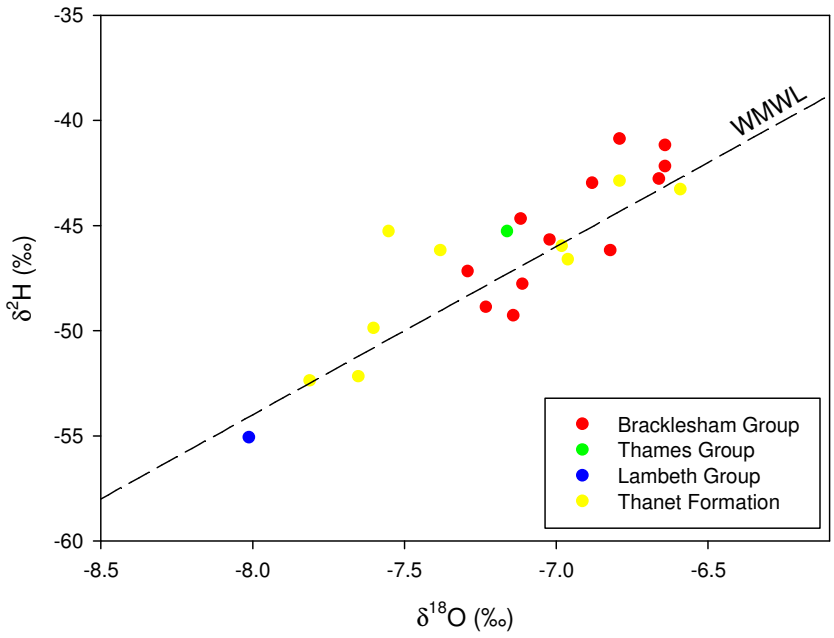

Figure 5.42 O and H stable isotopic composition of the London Palaeogene aquifer. WMWL = world meteoric water line.

the beds from which the samples were taken. The young Bracklesham Group beds, which crop out in the centre of the London Basin host the youngest groundwaters. The older, deeper beds host the older ground waters. The samples taken from the Thanet Formation represent a variety of ages, because samples were taken from these beds at outcrop and at depth. The oldest groundwater in this study was taken from the Lambeth Group. While this is not the oldest geological unit, the sample was taken from the centre of the basin, and represents the sample site furthest from the recharge zones.

The spatial variation of $\delta^{18}O$ and $\delta^{2}H$ is does not display a clear trend, which is partly due to lack of data around central London and Essex. However the most negative values are those in the north of the region. This is consistent with trends of Holocene groundwaters observed by Darling et al. (2003). In addition, the depth and age of samples need to be taken into account (see above and Figure 2.5).

The spatial distribution of ^{13}C in DIC can be an effective tracer of carbonate evolution (Clark and Fritz, 1997; Darling et al., 2005). Groundwater acquires dissolved inorganic carbon (DIC) through reaction with carbonate minerals, and with CO_2 derived from the overlying soil. The resulting C isotopic composition of the DIC represents a mixture of that of the soil (generally around -23 ‰) and that of a carbonate mineral source (ca. 0 ‰). Over time, excess CO_2 is consumed and solution precipitation reactions fractionate the $\delta^{13}C$ value towards the isotopic composition of the rock. Hence, more depleted values represent compositions less impacted by carbonate reaction.

The compositions in the Thames Palaeogene groundwaters range between -19.7 and -6.81 ‰ with a median of -17.1 ‰. This is a large range, and some of the sites are much depleted in $\delta^{13}C$, which should be expected in an aquifer which is not dominated by carbonates. The more depleted values suggest short residence times, whereas the less depleted values suggest longer residence times. The most depleted values tend to be found in the Bracklesham Group groundwaters (Figure 5.44), indicating a short residence time. The less depleted values tend to be found in Thanet Formation groundwaters, and indicate a longer residence time. This would be expected, especially as the highest value is found in the centre of the London Basin beneath the Clay.

5.5 CHEMICAL VARIATIONS WITH DEPTH

The groundwaters discussed above in Sections 5.1 and 5.2 are obtained from various formations within the London Palaeogene at various depths. As sample depth is not known, and the spatial variability is so great (see above) these data cannot be amalgamated to provide depth profiling.

Kinniburgh et al. (1994) analysed porewater from four newly cored boreholes in the Lea Valley. The authors obtained porewater bulked from each 0.5m length of core to provide a representative sub-sample. The results of the study are summarised below.

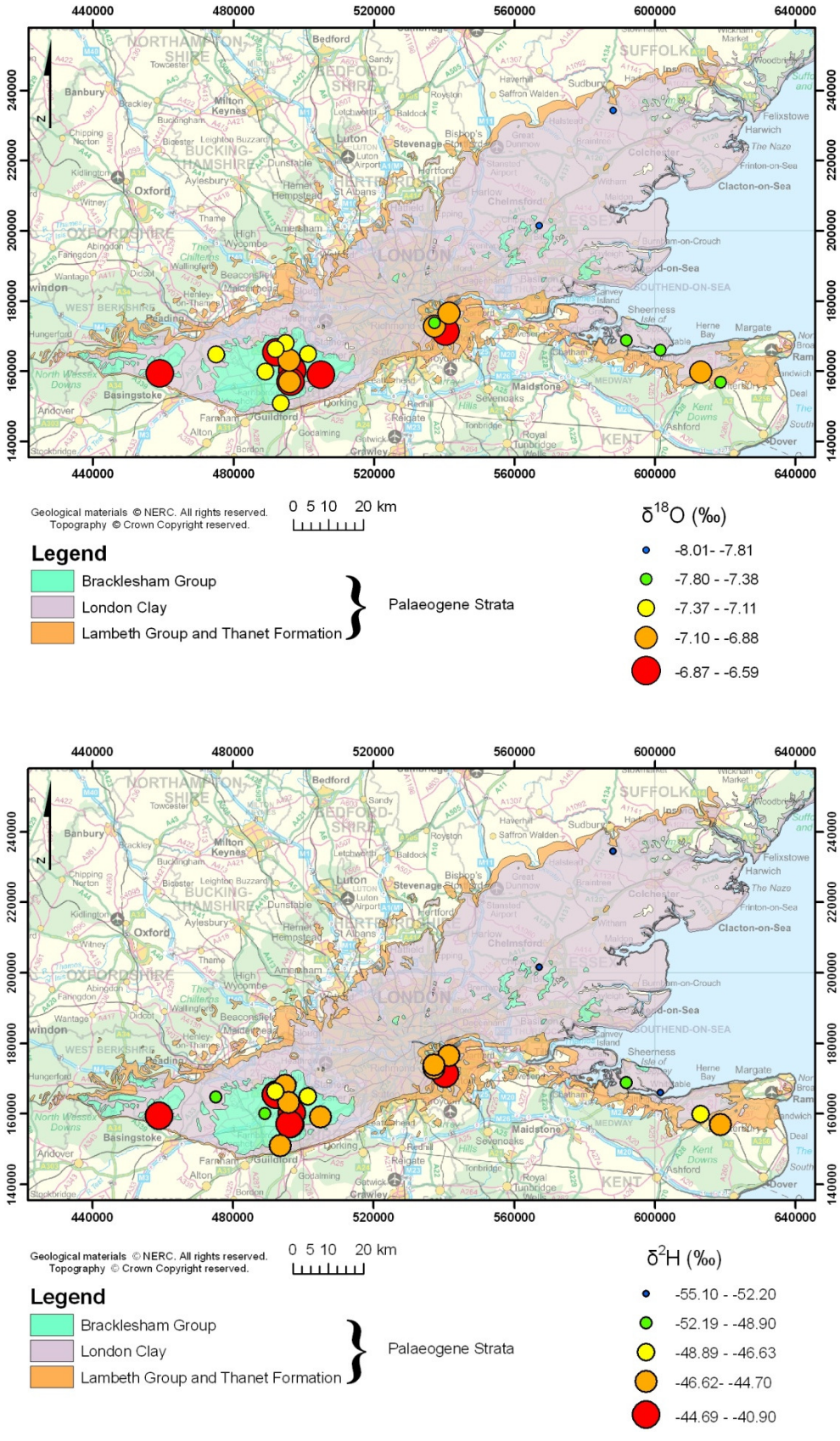

Figure 5.43 Regional variation of $\delta^{18}O$ and $\delta^{2}H$ within the London Palaeogene aquifer

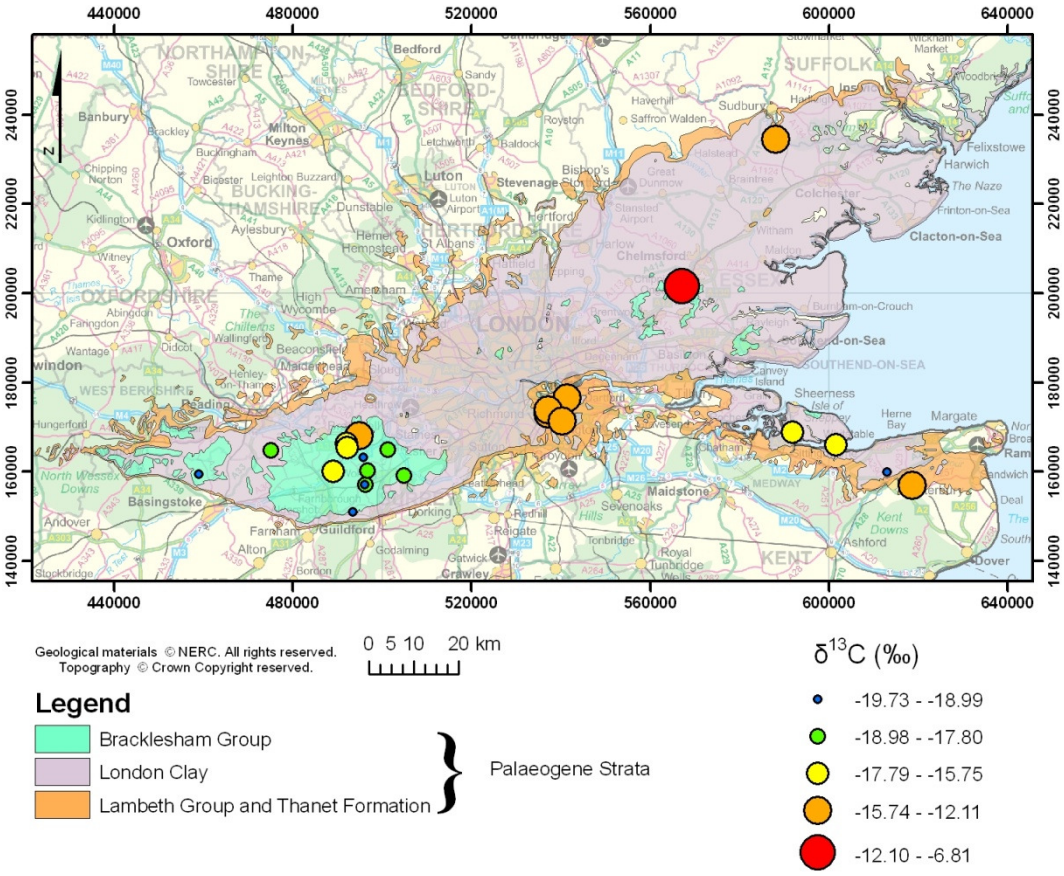

Figure 5.44 Regional variation of $\delta^{13}C$ within the London Palaeogene aquifer

Kinniburgh et al. (1994) found large variations in elemental concentrations and physico-chemical parameters between each site. The most notable feature was an acidic zone (pH = 3.5), ca. 2.5 m thick at the base of the Thanet Formation in one of the boreholes. This zone had correspondingly high concentrations of SO_4 (32800 mg L^{-1}), Fe (3000 mg L^{-1}), Al (930 mg L^{-1}), Mn (78 mg L^{-1}), Zn (36 mg L^{-1}), Ni (29 mg L^{-1}), Y (13 mg L^{-1}), Co (8 mg L^{-1}), Li (8 mg L^{-1}), La (1.2 mg L^{-1}) and Cu (800 µg L^{-1}). The other three boreholes did not have such low pH at the base of the Thanet Formation, although there were zones of low alkalinity. In two of the boreholes these low alkalinity zones corresponded to zones of high SO_4, which were also evident in Lambeth Group beds. The range of solutes present in elevated concentrations was found to be similar to that found in the pumped groundwaters in the Kinniburgh et al. (1994) study. The high concentrations and low alkalinity was attributed to pyrite oxidation. These results highlighted the sporadic distribution of this mineral as described in Section 5.2.

In addition to the above interpretation Kinniburgh et al. (1994) presented average values of the most abundant solutes in each stratigraphical unit. These have been used to create a Piper plot to present the water types in the four boreholes (Figure 5.45). This figure shows that the London Clay porewater is most variable with the water type ranging from Na+K-HCO_3 type, to Mg-SO_4 type waters. The porewaters from the Lambeth Group and Thanet Formation are generally Ca-SO_4 type waters and similar to the pumped groundwaters in this study (Figure 5.1).

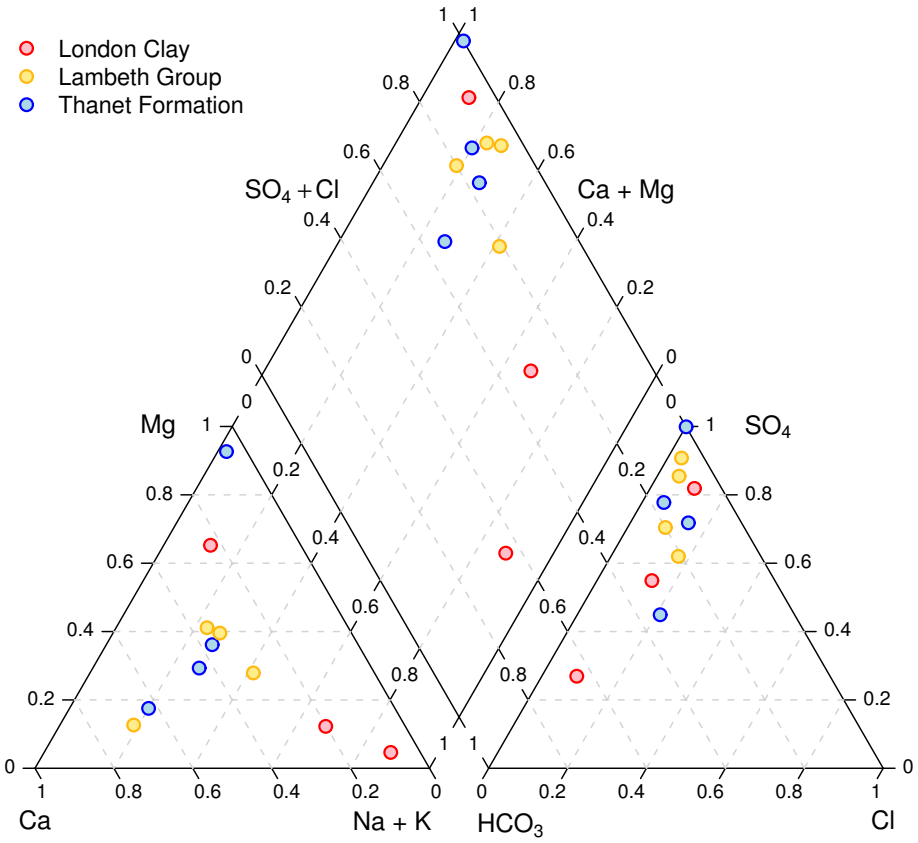

Figure 5.45 Piper diagram of average pore water concentrations in four boreholes in the Lea Valley (data from Kinniburgh et al., 1994)

It is difficult to describe graphically the vertical concentration distribution of the data, as there are only average measurements from three Palaeogene units. Figure 5.46 presents the Fe data showing that there are large variations in depth and spatially, which is typical of the pore water data and the results described above in Section 5.2.

5.6 TEMPORAL VARIATIONS

Data are available from the EA database for 10 sites within the Bracklesham Group, and one site within the Thames Group. Data are available for periods of two to seven years, and provide data for between five and 20 samples. Where recorded, there are variations in temperature and pH. These follow no distinct temporal trend, as is unsurprising given the dynamic nature of these parameters. Many elemental determinations also show variations in concentration, but display no temporal trend. There are, however, some notable exceptions.

At one site, ca. 3 km northwest of Bagshot, where the water is pumped from the Bagshot Formation, the Fe concentration in the groundwater increases over three years from 16 mg L^{-1} to around 24 mg L^{-1}. In the groundwater at the same site the SO_4 concentration increases from <10 mg L^{-1} to 40 mg L^{-1} (Figure 5.47), pH decreased marginally from 6.8 to 6.5, and dissolved O_2 reduced from 9.9 to 3.5 mg L^{-1}. This is likely indicative of pyrite oxidation. These trends are not seen in the other temporal data, in line with the likely sporadic distribution of pyrite throughout the Palaeogene strata. The pyrite will only oxidise if redox

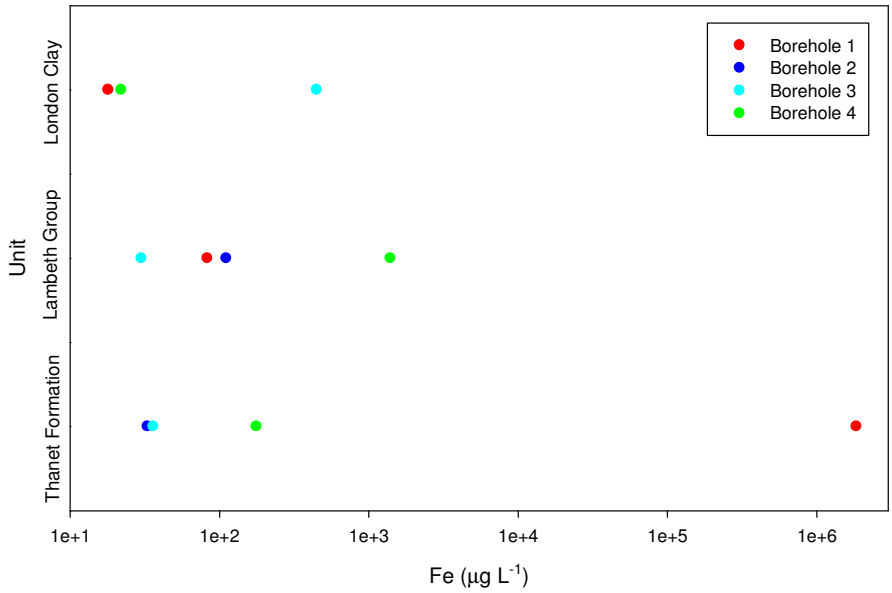

Figure 5.46 Variations of Fe with depth in four Lea Valley Boreholes (data from Kinniburgh et al., 1994)

conditions are suitable for it, for example due to dewatering or the introduction of an oxidising agent.

At all sites the NO_3-N was well within the drinking water limit of 11.3 mg L^{-1}, and increases in concentration were only marginal, at one site near Keston from groundwater from the Thames Group. The NO_3-N at this site increased from 2.5 to 3 mg L^{-1} over two years. The EA time series data for the Palaeogene aquifer cover mostly urban areas within the London basin. Anthropogenic sources of NO_3 in these monitored boreholes are therefore likely to be dominated by urban and industrial contamination, rather than that from agriculture.

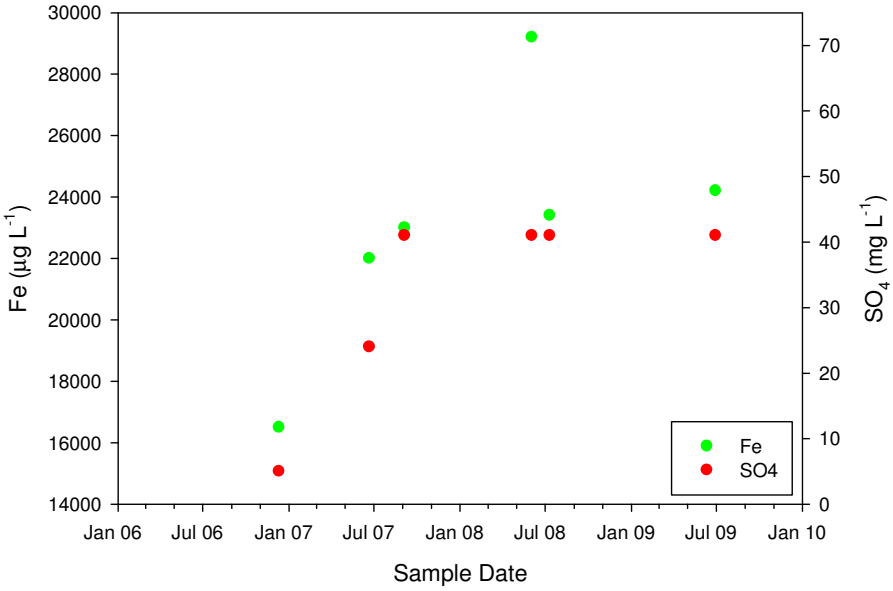

Figure 5.47 Fe and SO_4 concentrations over time at a site ca. 3 km northwest of Bagshot

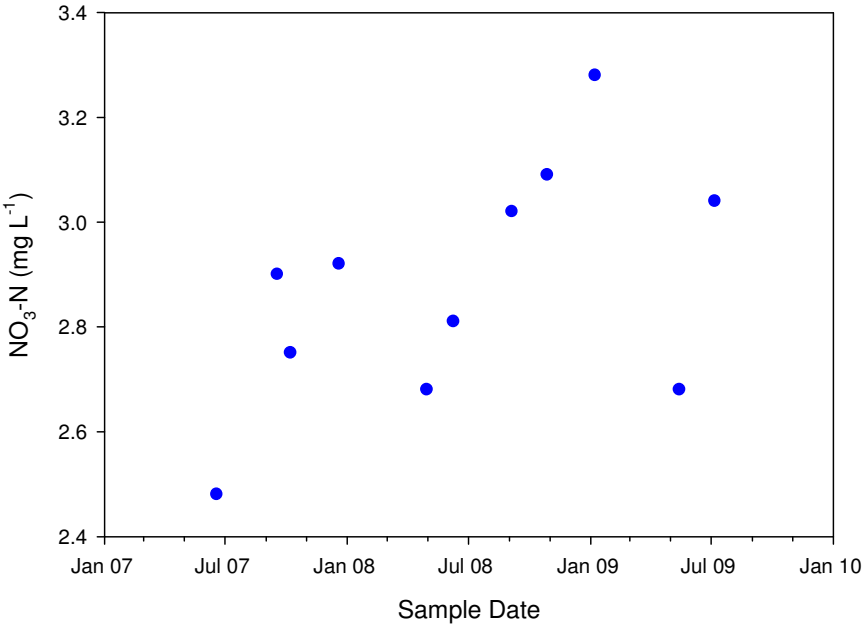

Figure 5.48 NO_3-N concentrations over time at a site near Keston

6 Baseline groundwater chemistry

6.1 REGIONAL BASELINE CHARACTERISTICS

The baseline chemistry of an aquifer is determined by a wide range of chemical and physical processes. The major source of most groundwater is rainfall. The London Palaeogene aquifers have hydraulic continuity with the underlying Chalk. Leakage between the Thanet Formation and the Chalk may modify the groundwater locally or regionally. A series of chemical reactions takes place during recharge; the most important of which are mineral dissolution and precipitation, in conjunction with mixing, redox reactions, ion exchange and sorption/ desorption reactions. These water-rock interactions are complicated by the heterogeneous nature of the London Palaeogene aquifer.

The waters in the study are taken from a range of geologies within the Palaeogene of the Thames Basin. Besides lithological variations between formations, there are variations within each formation, and hence the groundwaters that they host. While the water type was not distinct between formations (see Figure 5.1), the groundwater chemistry could generally be divided into two distinct populations: The Bracklesham Group, and the strata beneath this. It should be noted that there were only two samples taken from the Thames Group, and one from the Lambeth Group, making it difficult to draw firm conclusions from these data.

The concentrations of solutes in the groundwaters in the London Palaeogene can span many orders of magnitude. The observed ranges result from a number of factors, and natural geochemical reactions can account for the bulk of the observed variation. For most determinands the 95th percentile can be taken as a first approximation of the upper limit of the baseline range. This removes any obvious upper outliers for most determinands.

A notable exception to this is NO_3-N, for which the 95th percentile is 34 mg L^{-1}, and the 90th percentile is 18.1 mg L^{-1}. These values are in excess of the drinking-water limit (11.3 mg L^{-1}), and are highly unlikely to be naturally derived. It is unfortunate that the available time-series data do not include NO_3-N at such concentrations to examine change in NO_3-N over time. Neither do these time-series data extend back far enough to establish NO_3-N prior to urbanisation and industrial development. The distribution of NO_3-N concentrations presented on the log probability plot, and the distinct outliers on the box plot indicate a bi-modal distribution. Examination of the data reveals that most of the data are below detection and where detectable NO_3-N ranges from 0.03-55.7 mg L^{-1}.

High Fe and SO_4 concentrations are, at least partially, caused by oxidation of naturally occurring pyrite present within the Palaeogene strata. The reaction gives rise to acidic groundwater which can potentially dissolve other elements from the sulphide mineral or surrounding bedrock. However, whether groundwater compositions in the Thanet Formation can be regarded as baseline is open to question, since the oxidation reaction is largely in response to 20th century over pumping and dewatering of the aquifer (See Box 3.1 and Section 6.2).

Rainfall is an important control on the groundwater chemistry of conservative elements such as Cl. All of the groundwater Cl concentrations are much higher than the concentrated rainfall concentrations shown in Table 3.3. This suggests additional inputs of solutes, or more pronounced evapotranspiration than is typical in UK groundwaters. There are high concentrations of Cl around the north Kent coast, which correspond to elevated Na values and may indicate saline intrusion. However, the highest values of Na and Cl are found in the Lambeth Group sample, located near Margaretting [TL 67 01]. This is around 20 km inland and is therefore unlikely to have been affected by saline intrusion. This sample is of Na+K-C-

HCO_3 type and, as a groundwater exploited from beneath the London Clay is likely to be an older groundwater. The younger waters in this study area are dominated by Ca and HCO_3, as a result of the dissolution of calcite. As fresh groundwater flows into the centre of the London Basin it may come into contact with remnants of formation water, which may cause cation exchange of Ca for Na. The high Cl concentration in this sample may also indicate a formation water source.

Trace elements mainly derive naturally from the varied strata, their distribution being dependent on abundance as well as speciation and local aquifer conditions, including Eh and pH. Observed concentrations in many cases represent baseline compositions but some anomalous concentrations have been linked to contamination of the groundwater by various activities linked to urbanisation and population growth. The source of any contamination has been interpreted from geographic location, concentrations of accompanying solutes, local land-use and temporal variability.

6.2 EXTENT OF ANTHROPOGENIC INFLUENCES

Superimposed on natural baseline are anthropogenic influences. Anthropogenic influences can directly affect the groundwater chemistry via point sources or diffuse pollution. Additionally, anthropogenic influences can indirectly affect the groundwater chemistry, for example by physical processes such as abstraction.

While acid produced by pyrite oxidation is a natural process, the circumstances that have led to the oxidative weathering of this mineral in the beds beneath the London Clay are not. The abstraction of the underlying Chalk has caused the draining of the Palaeogene strata. In conjunction with tunnelling and borehole drilling the draining of the aquifer has allowed the entry of oxygen into the aquifer, not only has this compromised the water quality, but there are potentially hazardous problems to London's underground infrastructure (See Box 3.1). In order to establish the true baseline concentration of Fe, and other associated elements such as Mn, Co, Ni, within the London Palaeogene aquifer, pre-1800 analyses would be required to estimate the likely concentration of Fe and SO_4 released when the aquifer was confined and O_2 infiltration was limited.

Nitrate pollution is one of the largest problems facing unconfined groundwater in the UK; 60% of groundwater bodies in England may fail to meet the Water Framework Directive requirement of 'good' status by 2015 because of high NO_3 concentrations (Rivett et al., 2007). The main cause of these high concentrations is the development of intensive agriculture, which uses NO_3-rich fertilisers. Nitrate is extremely mobile and, while there are relatively few sites in the study area whose NO_3 concentrations exceed the drinking-water limit, there are signs that concentrations are increasing, and could exceed this limit in the future.

Anomalous concentrations of a suite of trace elements such as Zn, Cu, Cr, Mo, Mn and Ni can represent contamination from the wellhead pipework. However, no one sample contains particularly elevated concentrations of more than two of these elements. This indicates that metallic contamination is at a minimum in these groundwater samples, and the 95^{th} percentile is a good first approximation for baseline ranges of these elements, unless additional contaminant sources are present.

7 Conclusions

The London Palaeogene aquifer is variable in its geology and the groundwater it hosts is consequently variable in its natural character. The chemical compositions of the groundwaters have been characterised by investigation of the statistical distributions, mapping of the spatial variability, assessment of temporal changes, and interpretation of the predominant geochemical processes. For many analytes, the 95th percentile of the distributions has been taken as a first approximation of an upper limit of baseline concentrations as this serves to eliminate the most extreme outlier concentrations that likely represent a distinct population.

The main properties of the groundwater are determined by rainwater recharge reacting with the aquifer minerals. Of these minerals carbonates and pyrite are the dominant influence on the water chemistry, giving mainly Ca-HCO_3 to Ca-SO_4 type waters. There is a large spread of water types, which is a function of the bedrock variability and geochemical processes, but the major ion dominance cannot be distinguished between geological formations.

The minor and trace element concentrations tend to differ between formations. The data from the clayey Lambeth Group and London Clay Formation are limited, so cannot provide a useful baseline range. The upper sandy beds (Bracklesham Group) tend to be easily differentiated from the lower sandy beds (Thanet Formation). When concentrations are generally high in the former, they tend to be lower in the latter, and vice versa. However, it should be noted that within these trends there is much spatial variation.

Besides the geological variability between the Bracklesham Group and the Thanet Formation aquifers, the differences in the groundwater chemistry sampled from these beds may also be caused by the physical presence of the London Clay. When the aquifer was completely saturated (pre 1800) the Thanet Formation was confined by the London Clay. Recharge to the Thanet Formation was mostly via upwelling from the Chalk, which is in hydraulic continuity with the Thanet Formation. Since water levels in the Chalk were reduced by groundwater abstraction, the Thanet Formation also drained. This has allowed air access and made the Thanet Formation effectively unconfined, which in turn has initiated pyrite oxidation (see Box 3.1) which occurs sporadically throughout the formation. In comparison, the Bracklesham Group beds are unconfined and recharge occurs directly over the outcrop. The relatively impermeable underlying London Clay allows retention of this water in the Bracklesham Group. The Bracklesham Group beds are exposed to the air and pyrite oxidation can occur readily. The highest concentrations of Fe are found in the Bracklesham Group beds, which are generally oxic and often acidic.

Pyrite oxidation will continue until all the pyrite is consumed or the aquifer is allowed to completely fill, and the water reverts to a reducing condition. With recent controls over groundwater abstraction, water levels in the Thanet Formation are rising again, which may give rise to larger volumes of contaminated water, but in the longer term this may limit future oxidation reactions.

The abstraction of groundwater which drained the Thanet Formation indirectly contributed to the widespread poor water quality on account of the Fe concentrations. Despite the lower concentrations originating in the Thanet Formation, most of the waters tested would require treatment before they met the drinking water standard for Fe (0.2 mg L^{-1}) (OPSI, 2000). Additionally Mn concentrations generally far exceed the drinking water standard of 50 µg L^{-1}, and selected samples exceeded the Al drinking water limit of 200 µg L^{-1}, the Ni drinking water limit of 20 µg L^{-1} and the Pb drinking water limit to be effective as of 25th December 2013 of 10 µg L^{-1}.

This study indicates that the groundwater quality in the London Palaeogene is generally poor, although the groundwaters tested for the EA River Basin Management Plan indicated that most of the Palaeogene groundwaters in the London Basin are of "good" chemical status. As highlighted in this report, the highly variable nature of the groundwaters means that there are localised patches of poor groundwater. The poor groundwater quality is the reason for the scarcity of boreholes extracting groundwater from these layers. This is particularly so, given that the underlying confined Chalk aquifer has a much greater potential with large storage capacity and much better inorganic quality.

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